PB82-105230

Techniques for Handling Landborne Spills of Volatile Hazardous Substances

Battelle Columbus Labs., OH

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Sep 81

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TECHNIQUES FOR HANDLING LANDBORNE SPILLS OF VOLATILE HAZARDOUS SUBSTANCES

by

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Contract No. 68-02-1323

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Response needs of teams charged with handling spills of hazardous volatile materials on land are considered by Battelle-Columbus. Items of hardware which could be adapted or developed to improve spill response capabilities are suggested.

The report examines the available technology (and the lack thereof) being employed in current spill responses. An assessment of the phenomena that accompany spill volatilization is provided to determine and justify physical/chemical mechanisms that could potentially be used to control the hazards arising from volatility. As a result, approximately 60 items of hardware, which either exist or could be developed to improve hazardous volatile spill control responses, are discussed.

A set of spill scenarios is developed to compare the new suggested technology items with current spill response procedures.

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Vapors	Air pollution control	20M
Volatility	Emergency response	
Cryogenics		

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components requires a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solving, and involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources; for the preservation and treatment of public drinking water supplies; and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a vital communications link between the researcher and the user community.

This report covers a state-of-the-art survey and extension of techniques for the control of air pollutants from landborne spills of volatile hazardous materials. Included in the report is a discussion of the potential for the use of cryogenic techniques for control of volatilization.

In addition, 60 hardware items for better treatment of volatile spills that could readily be developed from current technology are presented. Those groups interested in improving current response techniques with respect to both environmental effects and spill response team safety will find this report to be of value. Further information on the subject may be obtained by contacting the Oil & Hazardous Materials Spills Branch, MERL-Ci, U.S. EPA, Edison, New Jersey 08817.

Francis Mayo
Director
Municipal Environmental Research Laboratory

ABSTRACT

Response needs of teams charged with handling spills of hazardous volatile materials on land are considered by Battelle-Columbus. Items of hardware that could be adapted or developed to improve spill response capabilities are suggested.

The report examines the available technology (and the lack thereof) being employed in current spill responses. An assessment of the phenomena that accompany spill volatilization is provided to determine and justify physical/chemical mechanisms that could potentially be used to control the hazards arising from volatility. As a result, approximately 60 items of hardware, which either exist or could be developed to improve hazardous volatile spill control responses, are discussed.

A set of spill scenarios is developed to compare the new suggested technology items with current spill response procedures.

This report was submitted in fulfillment of Contract No. 68-02-1323, Task 52, by Battelle Columbus Laboratories under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period January 30, 1976, to September 30, 1976, and work was completed as of November 1, 1977.

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ABBREVIATIONS AND SYMBOLS

d	Depth of spill
$\mathcal{D}$	Diffusion coefficient (cm^2/sec)
D_t	Total dosage (g/sec/m^3)
E_s	Heat capacity of soil (cal/gm-^oK)
H	Height of plume centerline when it becomes essentially vertical (cm, m)
ΔH	Latent heat of vaporization (cal/mole)
J	Flux (g/cm^2-sec)
J_h	Heat flux (cal/cm^2-sec)
k	Thermal conductivity (cal/cm-^oK-sec)
L	Length
P	Pressure
Q	Emission rate of vapor from a spill (g/sec)
Q_t	Total vapor release (g)
$q_{e,s}$	Heat transfer rate from earth (e) or from the sun (s) (cal/sec)
R	Gas constant
r	Characteristic surface dimensions (cm)
S	Solar heat flux (cal/cm^2-sec)
T	Temperature (^oK)
T_b	Boiling temperature (^oK)
ΔT	Temperature increment (^oK)
t	Time
$V_{f,i}$	Volume, (f) final volume, (i) initial volume
v	Wind velocity
x,y,z	Distances in a 3-dimensional system
$\sigma_{x,y}$	Dispersion coefficients in x direction, y direction (m)
ε	Dielectric constant
μ_x	Mean wind speed in the x direction (m/sec)
ρ	Density (g/cm^3)
χ	Mass concentration (g/cm^3)
BTU	British thermal unit
cfm	Cubic feet per minute
hp	Horsepower
LN_2	Liquid nitrogen
SAE	Society of Automotive Engineers

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CONVERSION FACTORS

To convert from	to	multiply by
British thermal unit (BTU)	joule	1.05435×10^3
	calorie (cal)	2.52×10^2
atmospheres (atm)	pascal (Pa)	1.01325×10^5
calorie (cal)	joule	4.184
foot (ft)	meter (m)	3.048×10^{-1}
foot^2 (ft^2)	meter^2 (m^2)	9.2903×10^{-2}
foot^3/minute (cfm)	meter^3/minute (m^3/min)	2.832×10^{-2}
degree Fahrenheit ($^\circ$F)	degree Celsius ($^\circ$C)	$T_C = (T_F - 32)/1.8$
degree Fahrenheit ($^\circ$F)	degree Kelvin ($^\circ$K)	$T_K = (T_F + 459.67)/1.8$
gallon (gal)	liter (l)	3.7854
	meter^3 (m^3)	3.7854×10^{-3}
gallon/minute (gpm)	liters/sec	6.309×10^{-2}
	meter^3/min (m^3/s)	6.309×10^{-5}
horsepower (hp) (550 ft lbf/s)	watt (w)	7.457×10^2
	cal/sec	1.7822×10^2
inch (in.)	centimeter (cm)	2.5400
	meter (m)	2.5400×10^{-2}
inch^2 (in^2)	meter^2 (m^2)	6.4516×10^{-4}
knot	miles/hr (mph)	1.15078
	kilometer/hr (km/hr)	1.852
mile (mi)	kilometer (km)	1.6093
	meter (m)	1.6093×10^3
miles/hr (mph)	kilometers/hour (km/hr)	1.6093
pound-mass (lb)	kilogram (kg)	4.5359×10^{-1}
pound-force (lbf)	newton (N)	4.4482
pound-force/inch (psi)	pascal (Pa)	6.89476×10^3
	atmospheres (atm)	6.8027×10^{-2}
ton (2000 lb)	kilogram (kg)	9.07185×10^2
yard (yd)	meter (m)	9.144×10^{-1}

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SECTION 1

INTRODUCTION

The problem of controlling air pollution from accidental releases of hazardous substances is acute since the response time required to prevent air pollution from occurring following a spill can be measured in minutes or even seconds. The situation is further complicated by the dispersed locations at which accidental spills occur and the need for mobilizing an appropriate control effort in accordance with geographical and pollution-type demand.

This study was conducted to: (a) examine the state-of-the-art techniques presently utilized to control and/or mitigate air pollution generated by the accidental release of hazardous gases or readily volatile hazardous substances that represent a potentially serious threat to human life and the environment, and (b) identify potential, practical, and economical technology that can be developed to reduce and/or eliminate the incidence of serious human health problems and environmental effects resulting from such air pollution. This study identifies and describes air pollution control technique concepts (hardware) that, if developed by further research and development efforts, would possibly result in a reduction or elimination of deficiencies in air pollution control techniques now utilized.

Concept definitions and inclusions/exclusions to the study are presented below.

DEFINITIONS

1. State-of-the-Art Technology is defined as commercially available technology now utilized in land spill responses, as well as technology classified in the final prototype (or nearly commercial) stage of development for control of air pollution or for removal or destruction of an air pollution source.

2. Control/Mitigation Techniques are defined as control technology hardware and the methodology (or processes) used for hardware operations in responding to episodes of air pollution generated from accidental releases on land of gases or readily volatile hazardous substances.

3. Hazardous Gas and Readily Volatile Hazardous Substances are defined as solid, liquid, or gas commodities that, upon accidental release or spillage, represent a threat to human life and the environment in the form of air pollution, explosions, and fire. The criteria for defining "readily volatile substances" were determined through

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comprehensive analyses of responses now utilized to control or mitigate releases of such substances.

INCLUSIONS/EXCLUSIONS

1. The hazardous gas and readily volatile hazardous materials covered in the study include only those pertinent materials listed in: (a) US EPA's "Designation of Hazardous Substances" list published in the December 30, 1975, Federal Register (1), and (b) the U.S. Coast Guard's "Chemical Hazard Response Information System (CHRIS)" hazardous chemical list (2). A special list, "Hazardous Chemicals That Produce Vapor," developed by the U.S. Coast Guard from the CHRIS 400 list, was extensively utilized as a guide for materials included in the study. This list (developed in report No. CG-D-46-75) of 103 substances (3) is composed of chemicals that produce a significant amount of vapor in a normal spill situation. The list contains chemicals shipped as gases and chemicals shipped as liquids but having relatively high vapor pressures at ambient temperatures.

2. The study was confined to accidents/spills of materials occurring on land for inplant, outplant (in transit), and fixed storage facility environments.

3. Transport spills covered in the study included railroad, pipeline, and truck modes of material transport (occurring on land).

4. The geographic scope included only spills occurring on land and specifically excluded accidents resulting in spillage of hazardous materials in harbors, the inner-continental shelf, commercial inland waterways, or other inland water bodies. The Federal Water Pollution Control Act Amendments of 1972 (subsection 311C1), and the Magnuson Act (50 USC 191 and 14 USC 88) have given statutory authority for response to hazardous chemical spills anywhere within the waters of the U.S. to the Coast Guard. The U.S. Coast Guard has sponsored several recent studies on spills in water (4, 5).

5. Radioactive materials were considered outside the scope of this study.

REPORT DEVELOPMENT

Through interviews with spill control officials, Battelle determined that less than 10% of the transportation-related spills involve fires of the materials involved. The incidents involving fire may reduce the hazards from the spilled materials, while also increasing the likelihood of spillage from adjacent unruptured containers. Since the control of fire, per se, is manageable by currently and commonly available technology (water and foam), and since the control of vapors, once released, is the subject of other ongoing research, this study did not examine vapor control concepts for spills involving fire.

The text of this report is divided into four sections. A brief discussion of each section follows.

Section 4. "Review of the Causes of and the Responses to Hazardous Landborne Volatile Spills." Spill reports and records are examined to determine the causes of spills on land of hazardous volatile materials, and the relative frequencies thereof. A summary of current field response technologies for controlling hazardous material vaporization is also presented. This summary was compiled from Battelle staff field experience and from spill response literature.

Section 5. "Phenomena of Hazardous Materials Volatilization." An understanding of the physical properties at work during a spill and in particular, the knowledge of the relative importance of the factors contributing to vaporization, must precede considerations of improved vaporization control technology. Physicists, chemists, and meteorologists cooperated to produce this section, which forms the basis for Section 6.

Section 6. "Proposed Landborne Hazardous Volatile Spill Vaporization Rate Control Concepts." Utilizing the information contained in Section 5, a number of idea sessions were held to generate concepts for new or improved volatilization rate control technology. The results of these sessions are presented.

Section 7. "Scenarios Utilizing New Vaporization Rate Concepts." Based upon actual spills, a number of scenarios involving landborne releases of hazardous volatiles were constructed. The application of existing technology is then compared with the use of the concepts of Section 6 to determine the possible utility of these concepts.

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SECTION 2

CONCLUSIONS

The current state-of-the-art for control of air pollution from spills of hazardous materials occurring on land is simplistic; the response being dependent upon local available materials (sorbents such as sand, straw, and flour) and equipment such as fire trucks (water hoses, pumps, protein-based foams), bulldozers, etc. Although not within the scope of this program, current response techniques and equipment leave much to be desired in terms of personal safety. The techniques now employed reqire close proximity to the spill, while the personnel protective gear provides inadequate protection for the hazards encountered.

Local fire departments are most frequently the first emergency units to arrive at spill sites. Because of their training, fire department response to spills often includes water flooding and, where immediately possible, vapor source removal. Precautionary population evacuation is frequently initiated by fire departments.

Where the local fire department is more sophisticated, foam blankets are sometimes applied to reduce evaporation and flammability hazards. However, final cleanup activities are generally not begun until emergency spill response teams are present. These activities may include sorption and burial.

Ratings of currently used spill response techniques are summarized in Table 1. The most effective procedures involve vapor source removal (reload to enclosed vehicles), deep soil burial, water flooding, and air curtain ignition systems.

There is significant room for improvement in cleanup technology for spills of hazardous volatile materials on land. This report addresses mechanical, chemical, and physical control, and techniques for applying ameliorative measures.

An examination of the various mechanical, chemical, and physical means of control indicates that lowering the temperature of the spill offers the most effective and universally applicable technique of dealing with volatile hazardous spills.

Solar heating of spills was found to be the predominant source of energy for the vaporization of spills (rain storms were not included in this analysis).

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TABLE 1. RATING OF EFFICIENCY OF CURRENT RESPONSE TECHNIQUES TO CONTROL EVAPORATION

	Slight Reduction	Moderate Reduction	Highly Effective
Reloading to Enclosed Vessels			x
Sumping and Trenching	x		
Wet Foaming		x	
Deep Soil Burial			x
Sorbents (Straw, Mulch, etc.)	x		
Water Flooding			x
Dispersants (On Thin Water Layers)	x		
Air Curtain Ignition Systems			x
Water Shroud Lines	x		
High-Pressure Water Fog		x	

Many spills would benefit from the application of more than one vapor suppression technique.

More than 60 techniques for delivery and deployment of coolants, tarpaulins, plastic sheets, and foams, by plane, helicopter, parachute, agricultural devices, skiploaders, cannons, mortars, catapult, line-gun, and crane, have been reviewed. No effort was made to select those delivery and deployment techniques deemed most promising.

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SECTION 3

RECOMMENDATIONS

This study has found there to be a critical absence of vapor suppression techniques and equipment. Because of this lack, unnecessary damage has resulted from the land spills of volatile hazardous materials. Current technology (e.g., water flooding), while adequate under some circumstances, has often produced unwanted hazardous side effects.

Battelle considers the use of cryogenic media to reduce or eliminate volatile emissions to be a most promising avenue of research, notwithstanding the potential hazards from the applied cryogen and from explosive boiling. The application of dry ice to reduce spill volatility has been used sporadically but with considerable success in vapor suppression. Systems that can project solid-slurries of granulated dry ice need considerable attention from researchers. Because of its very low boiling point, systems using liquid nitrogen (LN_2) can be used effectively to suppress vaporization of a very broad range of hazardous substances. Considerable attention must be paid to the potential problems of explosive boiling of LN_2 and the possible problem of condensation of free liquid oxygen.

In general, remotely operated systems to deliver the cryogens and adsorbing medium are needed. Systems such as air-driven seed-blower guns could deliver sufficient quantities of granulated dry ice to blanket a spill in a few minutes. Applicator guns and nozzles to deliver LN_2 and dry ice to a target are also recommended for further research.

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SECTION 4

REVIEW OF THE CAUSES OF AND THE RESPONSES TO HAZARDOUS LANDBORNE VOLATILE SPILLS

Before examining the needs for new technology, it is desirable to first examine the types of landborne spills of hazardous volatiles that are occurring, the nature of their causes, and current field response technology for controlling volatilization rate.

HAZARDOUS VOLATILES

The types of chemicals that are classified as hazardous volatiles include all high-vapor-pressure chemicals (those not boiling at ambient temperature and pressure) and cryogens (those boiling at ambient temperature and pressure). Chemicals that vaporize at a rate sufficient to have toxic or flammable concentrations also need to be considered, even though they are quiescent at ambient conditions.

A list of 200 chemicals that are transported on land and that present a hazard from volatilization when spilled was developed from U.S. Coast Guard and EPA lists of hazardous materials (1, 2, 3). A presentation and discussion of these chemicals is covered in Section 5.

SPILL CAUSES

The draft of a report was made available to Battelle by the Factory Mutual Research Corporation (FMRC) (6). With this report it was possible to examine the records of actual spills and their causes.

FMRC's breakdown of reported spills by operational area and by primary cause is given in Table 2. Most of the data collected by FMRC (6) on the incidence of spills directly reflects the lack of regulations with regard to reporting. The distributions given are those of reported spills, and are not necessarily the true distribution of national spill experience.

Frequency associations of primary and secondary causes, given in terms of percent of primary cause incidents in which the secondary cause appears (6), are given in Table 3.

The distribution of reported spills shows that 82% of the incidents are related to shipping. Specifically, in-transit spills total 57% while loading and unloading account for 25%. Although it is recognized that the reporting of spills is incomplete and that the FMRC data reflect this fact and hence may be biased, in view of the overwhelming incidence of spills that occur while

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TABLE 2. DISTRIBUTION OF REPORTED SPILLS OF HAZARDOUS MATERIALS

Operational Area		Primary Cause	
In Transit	57%	Non-Tank Rupture, Puncture	43%
Loading-Unloading	25%	Tank Rupture, Puncture	25%
In-Plant Process	10%	Tank Overflows, Leakage	17%
In-Plant Storage	7%	Hose Transfer System Failures	7%
		Other	7%

TABLE 3. FREQUENCY ASSOCIATION OF PRIMARY AND SECONDARY CAUSES OF HAZARDOUS MATERIAL SPILLS

Primary Cause	Secondary Cause
Tank Rupture, Puncture	Derailment, Collison and/or Overturn (54.7%)
Tank Rupture, Puncture	Body, Container Failure (33.4%)
Tank Rupture, Puncture	Sharp Object (15.5%)
Tank Overflow, Leakage	Personnel Error (29.6%)
Tank Overflow, Leakage	No Known Secondary Cause (26.4%)
Tank Overflow, Leakage	Mechanical Failure (18.5%)
Hose, Transfer System Failure	Hose or Coupling Failure (75.0%)
Non-Tank Rupture, Puncture	Sharp Object (31.1%)
Non-Tank Rupture, Puncture	Improper Loading (25.5%)

materials are in distribution systems, Battelle has concentrated upon this area of need.

CURRENT TECHNOLOGY

Based upon interviews with spill response personnel, Battelle staff experience, and spill literature, a number of currently available techniques

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suitable for vaporization rate control have been identified. These techniques are discussed in the following paragraphs.

Because of the lack of sufficient comprehensive spill incidence records, Battelle interviewed responsible individuals who are involved in immediate spill response actions. The effort centered upon spill contractors, government officials, and industrial environmental response personnel.

After consultation with government officials, corporate environmental managers, and insurance carriers, it was determined that water flooding is used on approximately 70% of the chemical spills, while approximately 20% are foamed over and 10% are treated with organic sorbents. Of the foaming procedures available, it has been found that the majority of fire control teams use a protein-based foam to blanket the volatile pools of chemicals. Reduction of spill area is employed in conjunction with the other techniques.

Vapor Source Removal

By far the most frequent response of spill control personnel to vaporization rate control is that of removal of the source of the vapor via offloading of the material from a damaged container to a more secure container.

Vapor source removal has also been used on hazardous materials which have already spilled. In these circumstances it is necessary to collect the spilled liquid in a contained area, and then pump the liquid into a closed container.

Foam Dikes

Foam diking is a relatively new technology, and thus experience in its use is limited. Not all surfaces are capable of serving as a base for foam dikes. There are two types of foam materials currently available.

Polyurethane Foam Systems--

Polyurethane foam systems appear to possess the necessary characteristics for field-operable units. The foam is formed by freon dissolved in one of the two reactants. As the polymerization proceeds, the heat of the reaction and the changing chemical composition causes the freon to volatilize and create the foam. The only work necessary is supplied by pressure, which expels and blends the two components. Other polymer foams require mechanical agitation and/or are open cell and thus a porous medium.

Polyurethane foams do have some limitations. On dry surfaces such as cement and asphalt, effective adhesion is easily achieved to contain a water depth of several feet. The ability to contain liquids behind barriers built of the foam on soil, however, depends upon the firmness of the soil. On hard-packed earth, effective control is often achieved, while on loose soil the fluid eventually works a path in the soil beneath the barrier. The polyurethane foam also performs poorly on vegetated ground and wet surfaces. The foams can also be used to seal storm drains even when moderate quantities of liquid are flowing through the drain gate.

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Inorganic Foam Systems--

The major item in this class of foam materials is a light-weight cellular concrete. Foamed gypsum is also an available material, as well as sodium silicate foam. The latter, however, requires mechanical agitation, is partially open-cell, and is subject to hydrolysis. All the materials above are formed by blending already formed, low-expansion foam into the appropriate slurry.

Wet Foams, Blanketing

A technique frequently employed by fire departments to decrease vaporization from hazardous chemical spills is the application of a foam blanket over the liquid. As will be discussed in Section 5, the foams in use today cannot effectively control vaporization. They can limit evaporation, however, by reducing heat transfer to the spilled material. Problems of foam usage include the possibility of foam ignition, the need to continually replenish the foam, and the susceptibility of foam to "lifting" and drift by winds.

Sumping and Trenching

By construction of sumps and trenches, it has been possible to reduce the surface area of a spilled material and thus reduce vaporization. Such construction also has enabled the collection and safe storage of the spilled material.

Deep Soil Burial

On occasion, spilled volatile materials have been buried on site, with the effect of greatly decreasing the rate of release of hazardous vapors to the atmosphere. This practice raises the spectre of other problems, such as groundwater contamination.

Sorption

A response technique that is frequently employed involves the application of a sorbent to the spilled material. Sorbent application can reduce the vaporization rate and can often result in the recovery of at least some of the spilled chemical. This technique is widely used because organic materials such as straw, charcoal, mulch, flour, and corn cobs are readily available. However, there are also commercially available reusable sorbents.

If the spent sorbent is recovered, the problem of disposing of the sorbed hazardous chemical, whether or not the chemical and sorbent can be economically separated, still remains. When the sorbent and hazardous material are separated, facilities must be provided for temporary (and perhaps long-range) storage and final disposal of the chemical. The failure to separate the hazardous chemical and sorbent simply adds to the bulk of the contaminated material and thus increases the storage and disposal problems.

Water Flooding

Most chemical spills are treated by water flooding, as a result, primarily, of the abundance of water-pumping equipment and of the fact that emergency response often involves fire departments. Water flooding of a spill often has some value:

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1. The spilled material can enter into solution with the water, thus decreasing the evaporation rate.

2. If it is not as dense as the spilled material, the water can cover the spilled material, thus decreasing the evaporation rate.

3. The water can disperse the spilled chemical, decreasing the atmospheric concentrations of the evaporant.

4. The water can be used to herd the spilled material into locations more suitable for cleanup activities.

Water flooding should not be applied to spills as a matter of course. In many cases, the application of water flooding has had severe side effects, including the pollution of nearby streams and the explosion of contaminants in sewer systems.

Controlled Ignition

Controlled ignition has been successfully employed on real spills, albeit infrequently. Flare stacks have been employed by natural gas companies to vent landfill areas around leaking gas pipes. Continual maintenance of flare stacks is necessary due to frequent flameouts. An air curtain destructor is available which, in essence, creates incinerator conditions in a trench so that the substance being burned is completely oxidized. The combustion products will contain essentially no visible emissions and, more importantly, no unoxidized hazardous volatiles. The air curtain destructors provide for excess air conditions, more turbulence, and increased retention time compared to simple open burning.

Burning is generally considered to be one of the most dangerous treatment operations. It should be attempted only after a careful review of alternatives and consideration of comparative risks. Open burning of spills usually requires burning agents to initiate and facilitate combustion. There are no standard, safe methods for igniting open spills.

RATING OF CURRENT TECHNOLOGY

While it is unlikely that all of the techniques that have ever been employed to control the evaporation of hazardous volatiles from landborne spills have been discussed in this section, from Battelle's experience and from interviews, it is believed that the majority (and certainly the most frequently used) have been addressed.

Table 1 has been prepared as a subjective ranking of the ability of the above-mentioned technologies to control evaporation. This table does not address itself to the probability that, given a spill, the technology would be applicable. Rather, it presents the expected efficiency of evaporation control, given that the technology is applicable.

EVALUATION OF NEEDS

From the information given in Table 1, it appears that there are three techniques which can be highly effective in controlling vaporization. They are vapor source removal, water flooding, and controlled ignition. Each of these techniques has limited applicability. Vapor source removal implies that it is possible to collect the spilled material and place it in safe containers. Water flooding, in essence, is simple dilution and can result in other problems. Controlled ignition is best left to isolated circumstances.

Spills of hazardous volatile materials must be dealt with quickly and effectively* to limit the impact on public health and the environment. At present, the arsenal of spill response tools is rather limited in applicability. The methods of controlling the vapor release of spills can be generalized as belonging to one or more of the following control categories:

1. Control by the use of mechanical means. By placing a barrier between the hazardous material and the environment, the release of evaporant to the air can be slowed or stopped. This includes reloading to closed containers, and covering the surface with tarpaulins, foam, etc.

2. Control by the use of chemical means. By addition of selected chemicals to the spill, the chemical or physical form of the spilled material is altered to control the release of the hazardous volatile. This includes water flushing, the addition of chemical neutralizers, and controlled ignition (which is the addition of oxygen at certain temperatures).

3. Control by the use of the physical properties of the spilled substance. By changing the conditions affecting the spill, it is possible to utilize the physical properties of the spill to control vaporization. This includes sorption, the lowering of the temperature of the spilled chemical in order to decrease vapor pressure, and the use of insulation to reduce the rate of heat transfer to the spilled chemical (this, in effect, also lowers the temperature of the spill).

There are a number of approaches as yet unexplored, by which vaporization rate control can be attained. The remainder of this report has focused upon the conceptualization of hardware (based upon existing technology for ease of development) for the control of vaporization rate. Before proceeding with a discussion of hardware, a study of the physical processes and their relative importance is presented in Section 5. The study has been used to help determine the parameters which are likely to have the most effect in hazardous volatile spill vaporization control.

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* The question of spill response personnel safety is somewhat peripheral to this study. It is recognized that current safety gear, even including experimental suits, is inadequate for some of the potential spills, since the demand-type regulators will allow infiltration of toxic gases. Therefore, many of the techniques presented rely upon remoteness for safety, although personnel safety equipment is not within the study scope.

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SECTION 5

PHENOMENA OF HAZARDOUS MATERIALS VOLATILIZATION

The purpose of this section is to examine a spill model and various possible vapor suppression concepts with respect to the physical and chemical phenomena involved during the spill and its suppression. The discussion has been purposely kept simple and the calculations are intended to produce order-of-magnitude answers. Careful simplification is both necessary and appropriate in order to obtain useful general observations which can be applied to many spills. More detailed models would, of necessity, involve the use of additional information specific to the properties and geography associated with a particular spill.

Battelle has selected 200 industrial compounds from the CHRIS Hazardous Chemical Data File (2) as representative of materials that present a hazard from volatilization when spilled. Their approximate physical properties will be used in numerical estimates and to determine the effects of various control concepts. The 200 chemicals are listed in Tables 4 through 8 (tables are at the end of this section), along with their selected physical and chemical properties, a description of the relative hazards associated with each compound, and information relating to the results of several potential vapor suppression concepts.

In the following discussion, a very qualitative description is given of some of the more important phenomena which may be observed during a typical spill. This will include an identification of physical processes that may be of importance in understanding the ultimate fate of the spill. A description of the behavior of the vapor plume formed by the spilled material is also included for completeness.

Several plausible approaches to the control of hazardous vapors associated with spills are examined by utilizing qualitative estimates of the magnitude of pertinent physical processes.

As a result of these analyses, Battelle believes that the concept of spill temperature reduction will reduce the human hazard associated with the widest variety of possible spill materials. This control technique can immobilize a spill and retard vaporization of the spilled material during removal and disposal. In addition, no examples were noted among the selected spill chemicals for which application of the temperature reduction concept as described would, in fact, worsen the environmental impact.

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Vapor containment, either with foam, a polymer layer, or water, is a viable concept for many spill materials. However, since this approach will not work for some spills and will be counter-productive for others, it is considered to be less useful than temperature reduction.

Some materials physisorb extremely well and adsorption could be an effective control procedure for these. For most materials, however, physisorption would be a marginally effective vapor suppression technique and therefore of still less potential use.

Finally, chemical neutralization is judged to be of quite limited utility primarily because only a small fraction of the test compounds can be treated in this manner. Those few chemicals that can be so treated require a number of different neutralization agents. In individual cases, neutralization might turn out to be the treatment of preference, but generally, this approach is considered to be of low potential.

SPILL DESCRIPTION

Low-Pressure Material

The chronology of a spill will be examined. The material spilled will be assumed to have a moderate vapor pressure (less than atmospheric) at ambient temperature; a material fitting this description might, for instance, be hexane.

As the material spills to the earth, some evaporates on the way down and a small quantity vaporizes on striking the ground, causing some cooling of the ground and the remaining liquid.

The liquid actually reaching the ground will soak into the soil and diffuse downward and transversely through the ground.* Some physical sorption occurs, binding the spilled material to the soil particles. Liquid spilled on pavement will spread and form very shallow puddles with slight penetration and some sorption by the pavement.

As the ground becomes saturated with the spilled material, the material cannot diffuse into the soil as fast as it is spilling. Because of the latent heat required by the vaporized material, the ground cools slightly, giving up sensible heat, and heat is conducted in (at a slow rate because the temperature of the spill differs little from its surroundings) from the surrounding earth. The formation of pools then begins. Material spilled on pavement will spread until it reaches soil and then will behave as described above. The flowing shallow puddle can gain heat rapidly from the air and pavement because the surface-to-volume ratio is quite large.

After the spill stops or slows, the pool evaporates because of heat radiated from the sun and conducted through the ground or pavement (plus some

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* Unless the spilled material is non-polar and the soil is wet — in which case the spill disperses on top of the soil.

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convection heat transfer from the air, though this is much smaller*). Either ground or pavement pools will tend to persist since adsorption increases the effective "heat of vaporization," i.e., sorbed spill material will evaporate more slowly.

After the pool has evaporated, the ground retains some of the spilled chemical which must diffuse out of the soil in order to evaporate. Evaporation of the final portions of the spill from the soil is the result of a complicated heat and mass transfer process. The evaporative process continues at an ever-decreasing rate. When the concentration of the chemical declines below some lethal level, the residues may be transformed by biological action, in addition to vaporization.

High-Vapor-Pressure Liquids

High-vapor-pressure liquids are here defined as those liquids for which the vapor pressure exceeds one atmosphere at ambient temperature. Thus, this material is boiling at the beginning of a spill. Therefore, boiling phenomena are of potential interest to one concerned with spills of high-vapor-pressure hazardous materials.

There are several types of boiling:

1. Nucleate boiling
2. Film boiling
3. Leidenfrost boiling
4. Explosive boiling

Explosive boiling is applicable only for a spill of a very high-vapor-pressure fluid (greater than atmospheric pressure) into another liquid; LNG into water is the classic case. In film boiling, heat transfer from the surroundings to the liquid is through a film of vapor, viz:

Liquid
Vapor
Hot Surroundings

By the same logic as is applied to explain the behavior of foam on vapor (see discussion below), the liquid-vapor interface will be unstable and boiling will occur. This results in the familiar rolling boil of water in a pot.

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* Convective heat transfer from the air will be much smaller than that conducted through the ground because the spill will be protected from the warmer air by a layer of cooler vapor, the conductivity of gases is typically two orders of magnitude smaller than that of solids, and the specific heat per unit volume of gases is typically three orders of magnitude smaller than that for solids.

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Despite the violent appearance of this type of boiling, heat transfer between the surroundings and the liquid is limited by the poor conductivity of the vapor film (relative to direct conduction between the liquid and the surroundings).

In nucleate boiling, the pool is quiescent with very small bubbles forming at nuclei on the surface of the hot surroundings. In this case, the rate of heat transfer to the liquid can be much larger than for film boiling, since in nucleate boiling the liquid is in direct contact with the surroundings.

Leidenfrost boiling is a special case of film boiling and occurs when drops of liquid are completely supported on a film of the vapor which separates the liquid from a solid surface. These liquid drops (e.g., cryo-fluids on pavement) are extremely mobile as the "vapor bearing" offers little resistance to movement. Thus, a spill of LNG (for instance) might spread a considerable distance as a liquid (carrying much hazardous material) and fail to be limited by available heat. Only sufficient heat to maintain the film under the material is required.

Each of these types of behavior is possible (as are more complicated situations that occur, e.g., when it rains) with the very high-vapor-pressure materials such as butane, ammonia, etc., which, when boiling, will lower the temperature of their surroundings substantially. Thus, a large enough spill could result in a pool that is in steady state with the ground and insulated from the atmosphere by cold vapor.

ATMOSPHERIC DISPERSAL

This section would not be complete without a description of the naturally occurring process by which the evaporated gases are diluted to safe levels and removed from the spill site. Qualitative discussion of the major features of transport and diffusion, together with means of estimating concentrations and dose, are presented. In addition to providing completeness to the discussion of spill chronology, this description gives a feel for the variety of atmospheric factors which may complicate simple-minded descriptions of plume phenomena.

Meteorological Factors

At the site of a spill of hazardous material, the principal interest in meteorological parameters concerns the material removal by atmospheric processes. Wind speed, wind direction, and atmospheric stability are important parameters determining the extent of atmospheric dispersion, while temperature, humidity, and precipitation are of lesser importance.

Dilution and Diffusion

Atmospheric dispersion of a material is controlled by two processes — dilution and diffusion. The greater the amount of air passing through a given volume, the more a material within the volume is diluted. Strong winds at a spill site will produce a lower concentration of the hazardous material downwind of the site. Atmospheric turbulence along the axis perpendicular to the

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wind produces horizontal and vertical diffusion. These turbulent eddies create an exchange between the air in the plume and the cleaner air outside, spreading the material over a more extensive volume. As a result, high concentrations of the material within the plume are reduced.

Turbulence has two causes — mechanical (exemplified by the eddies created when the wind flows past an obstacle) and thermal, which includes the eddies produced by rising hot air. In meteorology, atmospheric stability describes the ability of the atmosphere to enhance (unstable atmosphere) or inhibit (stable atmosphere) turbulent eddies. Under unstable conditions, the plume will diffuse rapidly. However, unstable conditions can also cause problems with an elevated plume as the plume may be carried downward momentarily, producing high pollutant concentrations at the surface.

Plume Rise

An important consideration in the dispersion of the plume from a spill is the plume rise. The higher a plume rises above its source, the greater the distance the material within the plume must travel downward to return to the surface. This increase in the distance the material remains airborne provides additional time for horizontal and vertical diffusion with the consequent decrease in atmospheric concentration of the material.

A plume hotter than the air in its vicinity will either:(1) rise until it cools to the temperature of the air around it, (2) rise until it reaches an inversion where plume temperature and ambient temperature are equal, or (3) be bent into the horizontal by the force of the wind. Strong wind, high ambient temperature, and the presence of inversions will reduce plume rise. Since plumes from evaporating liquids will be cool, the effective height of nonburning vapors will essentially be zero, and the plume will tend to hug the ground.

Ambient Concentration Prediction

Mathematical equations have been developed for predicting the downwind concentrations from a source emitting to the atmosphere. The general Gaussian diffusion equation is

$$C\ (x,\ y,\ z,\ H) = \frac{Q}{2\pi\sigma_y\sigma_z\mu_x} \exp\left[-\tfrac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]$$

$$\exp\left\{\left[-\tfrac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right] + \left[-\tfrac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\} \qquad (1)$$

where

$C(g\ m^{-3})$ is the mass concentration at a point x, y, z (where 0, 0, 0 are the source coordinates)

$Q(g\ sec^{-1})$ is the emission rate

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μ_x(m sec^{-1}) is the mean wind speed in the x direction affecting the plume

σ_y, σ_z (m) are dispersion coefficients in the horizontal and vertical directions, respectively

H(m) is the height of the plume centerline when it becomes essentially level (zero for nonburning spills).

The dispersion coefficients depict the diffusive characteristics of the atmosphere. The more unstable the atmosphere, the larger are the dispersion coefficients. They also are a function of distance from the source, increasing in magnitude with increasing distance. Variations of these general equations can be used to predict downwind concentrations under specified conditions.

Dosage

The foregoing equation predicts concentrations when the source is emitting at a continuous rate. Some spills emit all the pollutants instantaneously in a puff or cloud. For this case, the dispersion equation is altered to predict dosage — the integration of concentration over the time of passage of a plume or puff. The equation for the dose at the surface (z = 0) is

$$D_t(x,y,0,H) = \frac{Q_t}{\pi \sigma_y \sigma_z \mu_x} \exp -\tfrac{1}{2}\left[\frac{y}{\sigma_y}\right]^2 \exp -\tfrac{1}{2}\left[\frac{H}{\sigma_z}\right]^2 \qquad (2)$$

where

D_t = total dosage (g sec m^{-3})

Q_t = total release (g).

Field Applications

Several agencies charged with emergency action in response to spills have developed calculator or computer programs which use these dispersion equations to predict where the maximum atmospheric concentration will occur and how large this maximum will be. Extensions of the programs trace out the extent of the dangerous plume concentrations and which direction the plume will follow.

Observations of parameters needed by the program can be made at the spill site or interpolated from weather stations in the vicinity. One such plan requires that on-site observations be made of the following meteorological variables: wind direction, wind speed, percentage of sky covered by clouds, cloud height, cloud type, temperature, plume type, and precipitation or weather conditions.

HEAT TRANSFER

The following discussion will refer to spills of chemicals with a vapor pressure less than one atmosphere at 25°C. At steady state, an energy balance can be written for a spill which equates the energy lost by the vaporization process to the energy gained by conduction from the ground, convection from the atmosphere, energy input from rain or snow, and radiation from the sun.

Before examining the energy input from the surroundings in greater detail, the rate of vaporization from the spill will be considered.

In the absence of wind, a pool of high-vapor-pressure material will vaporize until its partial pressure above the pool surface attains the equilibrium vapor pressure of the material at the temperature of the pool surface. Equilibrium will not be achieved, however, since there is no container over the pool and the vapor will continually diffuse away. As the liquid vaporizes, removing energy (the latent heat of vaporization), it will lower the surface temperature of the pool. The presence of cooler, more dense material at the surface of the spill will tend to generate convection currents within the pool that will serve to reduce temperature gradients within the spilled fluid.

The steady-state condition will be characterized by a pool temperature lower than the ambient temperature (heat is entering the spill and being removed in the vapor). The vapor diffusion rate away from the pool will also play a major role in determining the steady-state condition. Thus, in general, a high-vapor-pressure material with a larger gas diffusion coefficient and a larger latent heat of vaporization will also establish a lower steady-state temperature.

Under wind conditions the vapor will be continually swept away from the pool. This forced convection process will enhance vaporization and produce a pool temperature lower than that found under still air conditions. Many other factors can complicate this simple picture. For example, if the material is spilled onto a grassy area, each blade of grass may behave as an evaporation surface so that the effective surface area is magnified. On the other hand, tall grass may reduce forced convection mass transfer and solar radiation input by shielding the spill from the wind and sun.

Quantitative Discussion of Evaporative Cooling

The model used for this calculation will be a pool of liquid of characteristic surface dimension (2r) with a wind velocity (v) passing over it. For typical spill sizes, uncontaminated air will enter from one side of the spill, pick up vapor as it passes over the spill, and leave the other side with essentially no large-scale turbulent mixing. Under these conditions, the slug of air can be regarded as stationary and the diffusion of the vapor into the atmosphere viewed as a situation in which the initial condition is air devoid of vapor. The air immediately above the spill can be regarded as near-saturated at all times since the maximum evaporation flux,

$$J\ max = \rho sat \left(\frac{RT}{2}\right)^{\frac{1}{2}} \tag{3}$$

(where ρsat is the saturated vapor density and R is the gas constant), is very large (it takes just a few picoseconds for this condition to be established). Thus, the rate of evaporation is limited by the diffusion or convection of the vapor away from the spill surface and not by the inherent rate of evaporation;

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for this reason, diffusion barriers which float on the liquid and in which the liquid is insoluble, or only slightly soluble, can have a major effect on the rate of evaporation.

Under the condition and the approximations described above, the diffusion problem becomes quite simple and the analysis appears in most elementary texts. The evaporation flux is

$$J = \rho sat \sqrt{\frac{\mathcal{D}}{\pi t}} \exp\left(\frac{-x^2}{4\mathcal{D}t}\right) \text{ g/cm}^2\text{-sec} \qquad (4)$$

where $\mathcal{D}$ is the diffusion coefficient, t the time after which the diffusion started, and x the distance from the surface. The total flux of material out of the liquid (at $x = 0$) is

$$J_o = \rho sat \sqrt{\frac{\mathcal{D}}{\pi t}} \text{ g/cm}^2\text{-sec.} \qquad (5)$$

For a slug of air passing over the spill in a time $t_o = 2r/v$, the average evaporative flux into the atmosphere is

$$\overline{J} = \frac{1}{t}\int_o^{t_o} J_o(t)\, dt = 2\rho sat \sqrt{\frac{\mathcal{D}}{\pi t_o}} \text{ g/cm}^2\text{-sec.} \qquad (6)$$

A typical value for $\mathcal{D}$ in gases is about 0.2 cm^2/sec. If the spill is about 50 meters long and a wind velocity of 10 m/sec (22 mph — a good, stiff wind) is assumed, i.e., $t_o \simeq 5$ seconds, the average evaporative flux is about 0.2 ρsat g/cm^2-sec.

Since $\rho sat \sim 10^{-3}$ g/cm^3 (for a gas of molecular weight 200 with vapor pressure of 2 psi at 25°C), then $\overline{J} = 2 \times 10^{-4}$ g/cm^2-sec.

Since the latent heats of most of the volatile hazardous materials under consideration range from 50 to 100 cal/gm, an average net heat flux input of $J_h \sim 2 \times 10^{-2}$ cal/cm^2-sec ~ 1 cal/cm^2-min is required to maintain the spill at constant temperature.

Having determined the approximate magnitude of heat flux needed to maintain a moderate vapor pressure spill at constant near-ambient temperature, it is possible to discuss the possible modes by which the spill can acquire this heat.

Ground Surface

Heat will transfer to the spill from the ground. At first, it will be the sensible heat of the soil near the interface (this could cause boiling in some cases). The heat supplied by conduction through the ground will decrease with time as described by a transient heat transfer equation.

Heat Transfer to the Spill From the Atmosphere

When there is no wind, the heat transfer from the atmosphere to the spill will occur via conduction through the vapor-air mixture over the spill. When

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there is a wind, heat will be carried to the spill by convection. In either case, the rate of heat transfer from the atmosphere to the pool is orders of magnitude less than that from the ground.

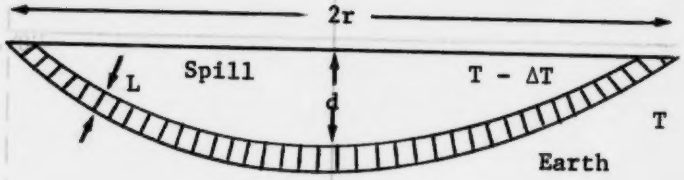
Rain

Additional heat can be supplied to a spill by rainwater (or water introduced by attempts at dilution) in the amount of one cal/gm water/°C.

Comparison of Heat Input From the Sun and the Land

It is instructive to compare the energy available to the spill as sensible heat of the earth to the energy available as a result of direct solar radiation. The specific heat of soils is about 0.2 cal/g/°C and the bulk density is approximately 1.2 to 1.6 g/cc. When the latent heat of a spilled material is 75 cal/g , then approximately 375 g of earth would have to be cooled an average of 1°C to evaporate 1 gram of spill. Very roughly, then, a volume of soil 10 m x 10 m x 1 m would have to be cooled an average of 1°C to evaporate 100 gal of spilled material.

Consider a simple geometry (that of an ellipsoid) in which a spill fills a circular depression of radius r (as seen from above) to a depth d. The



maximum rate of radiant energy transfer from the sun to the spill is

$$q_s = S \pi r^2 \text{ cal/min.} \tag{7}$$

The solar flux, S, will be assumed to be approximately one-half the solar constant, or approximately 1 cal/cm^2-min.

If it is assumed that the spill is evaporating slowly, is ΔT below the average soil temperature, and that the soil temperature gradient can be approximated as ΔT/L, then, for soil conductivity of 0.003 cal/(cm-sec-°K), the rate of heat transfer to the spill from the soil is

$$q_e = kA\frac{dT}{dx} = (0.003)(60)\,\frac{\pi r^2 \Delta T}{L} \text{ cal/min.} \tag{8}$$

Here, r has been assumed to be much greater than L or d, i.e., the area of the interface between the spill and the soil is approximately πr^2. Thus, the ratio of heat supplied by the earth to that supplied by the sun is

$$\frac{q_e}{q_s} = \frac{0.18\ \Delta T}{L}\,. \tag{9}$$

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If a hemispherical depression had been assumed instead of a very flat one, the ratio would be twice this value. The approach is believed to be a satisfactory way of estimating the relative importance of soil conduction and solar radiation. The energy given up by the earth in cooling the shell of thickness (L)surrounding the spill, by an average of $(\Delta T/2)$ is

$$E_{soil} \sim 0.3\ \pi r^2\ L\Delta T \text{ cal.} \tag{10}$$

$\pi d^2(r-\frac{d}{3})$

This value will be compared with the energy required to evaporate the entire spill obtained by multiplying the volume of the spill, $\pi d^2(r-d/3)$, by an appropriate average latent heat of vaporization (100-150 cal/gm) and by the density (0.7-1 gm/cm^3); thus

$$E \sim 106\pi d^2(r-d/3)$$

For a large spill that is 1°C lower in temperature* than the surrounding soil, the rate of heat conducted through the soil is about equal to 36% of the maximum provided by solar radiant energy when the soil has given up enough heat to evaporate 0.2/r percent of the total spill. Thus, it can be seen that, for a large spill, solar radiant energy can be a more important factor in providing the heat needed for evaporation than thermal conductivity through the earth. Of course, the existence of an opaque vapor cloud over the spill can complicate the solar radiation effects.

FACTORS INVOLVED IN SOME VAPOR CONTROL CONCEPTS

Many methods have been tried or proposed for the control of the release rate of vapors from evaporating liquids. It is instructive to examine the mechanisms by which these proposed methods work, so as to help in the determination of the relative worth of the various techniques.

Diffusion Barriers

A diffusion barrier reduces the net evaporation rate by hindering or retarding the passage of molecules through it to the vapor phase or by reducing the spill area available for evaporation. The barriers cannot alter the equilibrium vapor pressure, but will act to slow the rate of approach toward the equilibrium. Barriers can be mechanical devices which enclose and seal off the spill area or floating objects such as "ping-pong" balls, or they can be an immiscible liquid layer which can be spread over the spill, a surfactant, or a light foam.

At present, experiments are being conducted on the use of foams on spills as a means of vapor containment (4). A cross-section of the foam-blanketed

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* This number was chosen to represent a steady-state condition (where the pool temperature is the result of the effects of evaporation, solar radiant energy, and conduction) and not the initial conditions. The temperature difference is taken as representative of that of a chemical with a moderate vapor pressure.

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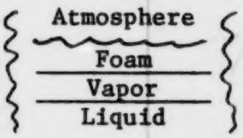
spill would appear as shown below.



A goal of the foam-blanketing experiments is to produce this stable layered configuration. Often, however, the vapor tends to bubble up through the foam (vapor also diffuses through the foam, but this is a different problem). This is a problem in classical mechanics called the Taylor instability. The foam-vapor interface will be stable (i.e., vapor will not tend to break through the foam) when the mass density of the foam is less than that of the vapor, i.e., if the relative density of the vapor is 2 (relative to air), then foam containment will be successful if the density of the foam is less than 2.

Physical Adsorption

Physical adsorption describes an interaction between a molecule and a substrate surface caused by secondary attractive forces (van der Waals). It does not involve the transfer of an electron or electrons between the surface and the molecule. (When electron transfer occurs, the process is called chemisorption and amounts to a chemical reaction between the surface and the molecule.) Physical adsorption is reversible with the addition of a modest amount of thermal energy (usually less than 4000 cal/gmol); chemisorption requires the breaking of chemical bonds for reversal and requires correspondingly larger amounts of thermal energy. An example of "physisorption" is the adsorption of organic molecules on activated charcoal; chemisorption might be exemplified by the rusting of iron.

The forces responsible for physical adsorption are associated with electrical dipoles. There are both first-order and second-order forces. First-order interaction involves molecules with a permanent dipole moment. When such a molecule approaches a surface, an image dipole is induced at the surface, which results in an attraction between the surface and the molecule. At short distances, electronic repulsive forces come into play, resulting in a thin surface layer in which the molecule may be trapped.

Molecules lacking a permanent dipole moment generally possess some electronic polarizability. That is, they can display an induced dipole moment. Spontaneous fluctuations within the molecules result in transient dipole moments, which generate image dipoles in the surface and a consequent attractive force between the surface and the molecule. Because this force depends on spontaneous charge fluctuations, its magnitude is smaller than for those molecules with a permanent moment. Generally, the strength of the bonding induced by such forces is proportional to the polarizability of the molecule.

Thus, molecules with a very large dielectric constant (which implies a permanent dipole moment for the molecule) will physically adsorb well. For molecules with no permanent dipole moment, those with the largest dielectric

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constants will be likely to form the strongest bonds.*

With this physical background in mind, the volatile hazardous chemicals for which dielectric constants (ε) are listed were grouped according to the value of this parameter. Compounds with a very large dielectric constant ($\varepsilon > 30$) were judged to have a large dipole moment and probably a large polarizability. It was expected that these compounds would adsorb very well and they were therefore rated as "very good." Smaller dielectric constants ($10 < \varepsilon < 30$) were judged to be due to smaller permanent dipoles, and smaller polarizability. It was expected that chemicals with ε in this range would be moderately attracted to the adsorbing medium. Thus, these materials were rated as "good." Still smaller dielectric constants ($\varepsilon \sim 5$) were judged to be a reflection of either large dynamic polarizabilities with no permanent dipole, or small permanent moments with perhaps small polarizability. Materials with ε of about 5 were rated as "fair." Dielectric constants of the order of 2 reflect the lack of a permanent dipole moment and a relatively weak electronic polarizability. Materials with ε in this range were rated as "poor."

Dielectric constants could not be found in the literature for all the materials listed. For some chemicals, estimates of the efficacy of adsorption as a control mechanism were made by using related criteria. In some cases, structural similarities were used. As an example, since the cyanide group has a large permanent dipole moment and is quite polarizable, compounds with a cyanide group were rated as "very good" candidates for control by adsorption. On the other hand, since alkanes and alkenes have very small dipole moments and small polarizabilities, adsorption was assessed to be a "poor" means of control. Permanent dipole moments have been tabulated for some of the compounds. Although they do not reflect the dynamic electronic polarizability as does the dielectric constant, they were also used to estimate the relative effectiveness of adsorption as a method of control.

It must be recognized that ratings based on the size of the dielectric constant are relative and subjective. That is, it can be estimated on the basis of dielectric constants that a material with $\varepsilon \sim 10$ will be better adsorbed on a high-surface-area medium (e.g., activated charcoal) than a material with $\varepsilon \sim 2$. Because of other factors involved in the adsorption process, however, the order might be reversed. The estimated ratings must be checked experimentally. In addition, it could well be that even if the material with $\varepsilon \sim 10$ does adsorb much better than that with $\varepsilon \sim 2$, physical adsorption may be a perfectly adequate control mechanism for the material with $\varepsilon \sim 2$. This, too, would need to be evaluated experimentally.

Effects of Temperature Reduction

Reducing the temperature of a potentially hazardous spill can be advantageous in several ways. It can:

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* There is not a linear relationship between the static dielectric constant and the molecular dipole moment; however, the dielectric constant is a monotonically increasing function of the molecular dipole moment.

- Increase the viscosity and thereby effectively help to contain the spill and to restrict thermal transfer by convection within the spill. If the material spilled freezes at the lowered temperature, the boundary of the spill can be maintained and, possibly, the rupture from which the spill is coming might be sealed temporarily.

- Decrease the vapor pressure, thereby reducing exposure to the spill fumes and probably reducing the explosion and flammability hazard.

There are numerous coolants which might be used to reduce the temperature of a spill. Here, two are considered: dry ice and liquid nitrogen (LN_2). These were chosen because they are readily available, provide low temperatures, are nontoxic, and do not support combustion. (CAUTION: Under no circumstances should liquid air be used in lieu of liquid nitrogen. Since nitrogen boils at a slightly lower temperature than oxygen, as the liquid air boils, nitrogen will boil off preferentially, potentially leaving behind extremely hazardous concentrations of liquid oxygen and oxidizable material. The concept of the use of liquid nitrogen must itself be tested experimentally to determine if an oxygen concentration builds up by condensation from the atmosphere.)

It is easy to determine whether the reduced temperature provided by dry ice or LN_2 could immobilize the spill by comparing the freezing point of the spilled material with the boiling point of LN_2 or with the sublimation temperature of dry ice. An accurate value for the reduction in vapor pressure resulting from the reduced temperature would require accurate vapor pressure tables for each of these materials. However, it is possible to estimate the vapor pressure using thermodynamics and some reasonable approximations.

Clapeyron's relation for a liquid phase in equilibrium with its vapor is (approximately)*

$$\frac{dP}{dT} = \frac{P\Delta H}{RT^2} \qquad (12)$$

where P is the vapor pressure, ΔH is the latent heat of vaporization, R the gas constant, and T the absolute temperature. This relationship is approximate in that it assumes that the vapor behaves as a perfect gas and that the volume of one mole of liquid is negligible with respect to the volume of its vapor. It is a reasonable approximation to take the latent heat to be constant, in which case Calpeyron's relation may be integrated to give

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* Clapeyron's relation for any first-order transition is

$$\frac{dP}{dT} = \frac{\Delta H}{T(v_f - v_i)}$$

where v_f and v_i are the final and initial volumes of material, respectively. If the volume of the liquid phase is neglected and the vapor treated as an ideal gas, the approximate Clapeyron's relation is obtained.

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$$\ln \frac{P}{P_o} = -\frac{\Delta H}{RT} \qquad (13)$$

where P_o is a constant of integration. P_o can be determined by observing that, at the boiling point, P is one atmosphere (14.7 psi). Thus,

$$1\ (\text{atm}) = P_o e^{-\Delta H/RT_b} \qquad (14)$$

where T_b is the boiling temperature of the liquid. It turns out that, for most materials,

$$\frac{\Delta H}{T_b} \approx 20\ \text{cal/mole-degree.} \qquad (15)$$

This is referred to as Trouton's rule. Since $R \approx 1.98$ cal/mole-°K, then

$$P_o \approx e^{10}\ (\text{atm}). \qquad (16)$$

Writing the integrated Clapeyron relation, Eq. 13, for another temperature, T'

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$$\ln (P'/P_o) = -\Delta H/RT' \qquad (17)$$

and rearranging and combining Eq. 17 with Eq. 13 yields

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$$(P/P_o) = (P'/P_o)^{(T'/T)}. \qquad (18)$$

If T' is taken to be the boiling temperature, T_b, then P' = 1 and

$$P = P_o(P_o)^{-T_b/T} = P_o^{-[(T_b/T)-1]}. \qquad (19)$$

Because of the use of Trouton's rule and other approximations, P has been calculated at the dry ice sublimation temperature and the LN_2 boiling temperature as a function of T_b for values of P_o equal to e^{+9} and e^{+11}. These calculations should bracket the correct value of P.

The values obtained from Eq. 19 are presented in Figure 1 to illustrate the possible effectiveness of vapor pressure reduction techniques using dry ice. Estimates of the vapor pressures obtained in this manner are displayed in Tables 4 through 8.

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It is instructive to estimate the quantities of LN_2 or of dry ice needed to cool a spilled chemical to the control temperatures implied by the applied coolant. The latent heats of sublimation and vaporization of dry ice and LN_2 are, respectively, 90 cal/gm and 48 cal/gm, so that a given weight of dry ice is nearly twice as effective a coolant as an equal weight of LN_2. To cool one pound of benzene to the dry ice temperature, for example, will require 0.7 pound of dry ice and to cool the benzene to the LN_2 temperature will require 1.8 pounds of LN_2. (This, of course, does not include the amounts needed to compensate for the increase in the heat transfer rate to the spill.) If it is only desired to freeze the benzene, 0.3 pound of dry ice and 0.5 pound of LN_2 will be required.

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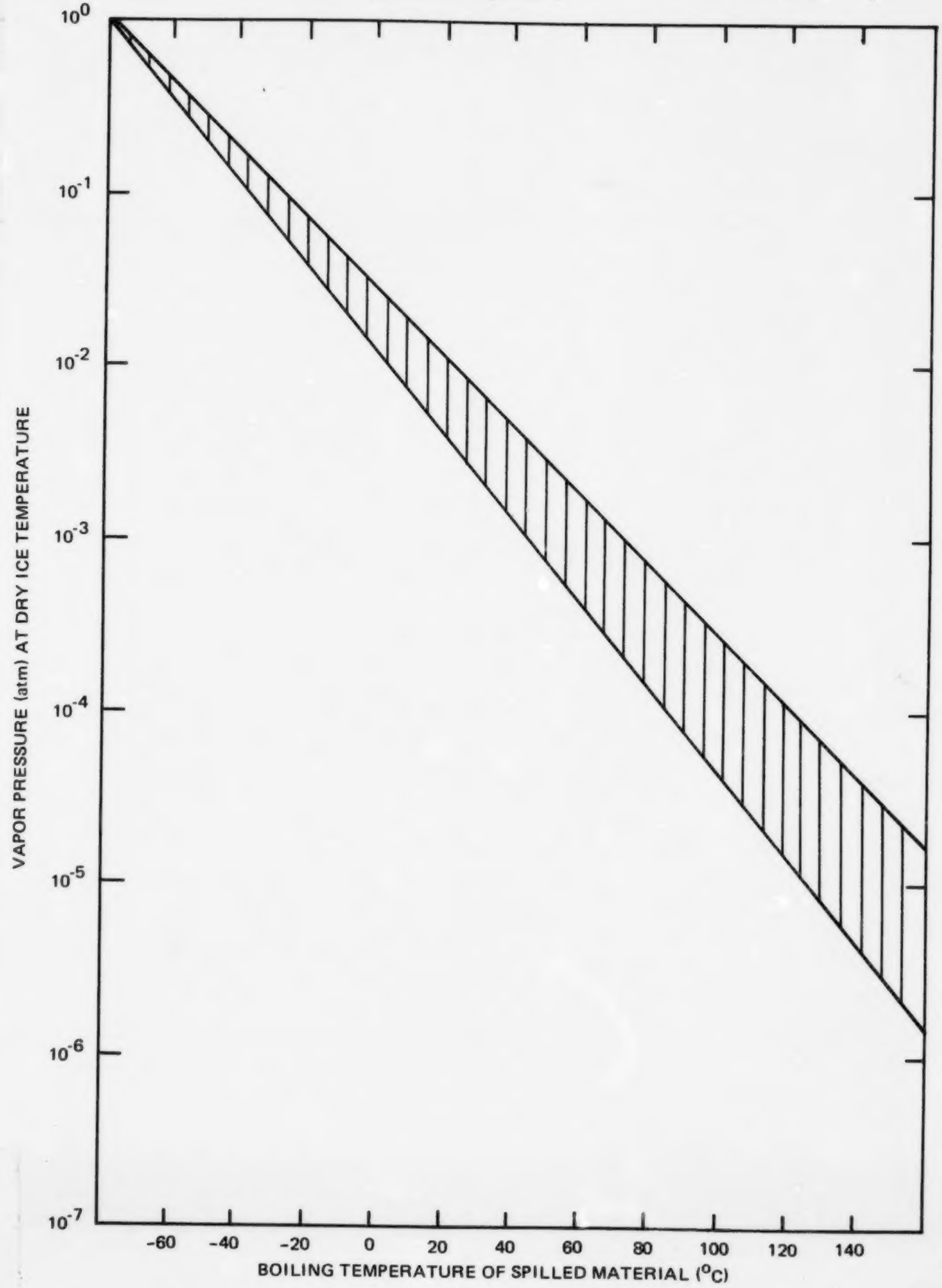

Figure 1. Band of expected vapor pressures at dry ice temperature of spilled materials versus their boiling temperatures.

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Effects of Viscosity

Another physical aspect which may enter the problem is that of the viscosity of the spill. An inviscid fluid will spread quickly, gaining surface sensible heat at the periphery of the spill. A more viscous fluid tends to spread slowly, limiting heat transfer to the fluid. Thus, vapor control can be achieved by the addition of "thickeners" or gelling agents to the spill, or by otherwise constraining the spread of the liquid.

Chemical Neutralization

The reaction of the spilled chemical with other compounds to produce a less hazardous product or a product with a lower vapor pressure will reduce the danger of cleaning up spills of certain materials. However, this approach is fraught with risk of increased environmental insult. The neutralizing chemical reaction will release heat which could result in vaporization of unreacted parts of the spill. Temporarily, at least, the plume will then be more hazardous than if nothing had been done. Moreover, the added compound and/or the product (both of which must be low-vapor-pressure compounds of lower toxicity for the control process to represent an improvement over doing nothing) may represent toxic effluents to nearby land, streams, and lakes. For instance, neutralization of an HCN spill with an aqueous solution of caustic soda will produce an aqueous solution of sodium cyanide and caustic soda, which must be prevented from entering neighboring waterways. Furthermore, the reacting agent needed will be very specific to the particular material spilled. Addition of a dilute acid to a spill (a proper course of action for a spill of basic material) would clearly be counterproductive if the spilled material were also acidic. Neutralization of plastic monomers by polymerization requires the addition of catalytic agents. While a single catalyst might be found that would work for most of the monomers used today, such a catalyst is as yet unknown.

As evidence of the variety of chemical control agents which might be needed to effect vapor suppression by chemical neutralization, the following tabulation is presented:

Chemical Class	Reagents Needed For Neutralization
Bases (e.g., amines)	Acids or acidic salts
Acids	Bases or basic salts (e.g., caustic soda, lime, slaked lime, Portland cement, soda ash)
Aldehydes Ketones	Amines (e.g., hydroxylamine)
Cyanogen chloride Nitrosyl chloride Phosgene Oxides	Caustic soda
Plastic monomers	Peroxides

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CHEMICAL AND PHYSICAL PROPERTIES OF SELECTED VOLATILE HAZARDOUS SUBSTANCES

A group of 200 industrial organic and inorganic chemicals has been selected for consideration of possible concepts for vapor control during a spill. The criteria for choosing the chemicals were that they had an appreciable vapor pressure and that the vapor would be likely to represent a toxic or explosive threat to human life. The list of 200 is not all-inclusive, but was deliberately chosen to be sufficiently large that a potential spill control scheme could be tested to determine the breadth of its applicability.

The 200 chemicals selected are listed in Tables 2 through 6. The chemicals are grouped in these tables by vapor pressure as shown below.

Table 2 - Compounds with boiling points of $25^{o}C$ or lower
Table 3 - Compounds with boiling points between $26^{o}C$ and $70^{o}C$
Table 4 - Compounds with boiling points between $70^{o}C$ and $125^{o}C$
Table 5 - Compounds with boiling points between $125^{o}C$ and $200^{o}C$
Table 6 - Compounds with boiling points above $200^{o}C$.

In these tables, several important physical and chemical properties, hazard ratings, and the effectiveness of potential control procedures are displayed, as available for each of the chemicals. The physical properties listed include the boiling point (in ^{o}C), the vapor pressure (at $80^{o}F$), and the relative density of the vapor (relative to air as unity) at ambient temperature. It is interesting to note that the vapor from some of these materials is several times more dense than air. For spills of these compounds it is possible (where the foam density is sufficiently small) that foam can be used to retard vaporization without vapor breakthrough.

The chemical properties listed include a qualitative description of the solubility of the chemical in water and a notation of the primary functional groups represented in the chemical. The first of these properties is quite important since many spills are first treated by flushing with water. In addition, the solubility in water is relevant to potential plume control methods which use an aqueous diffusion barrier. The variety of groups appearing in the second column of chemical properties illustrates the difficulty of applying chemical control techniques to spills.

The hazard ratings rank the various chemicals qualitatively on a scale of 1 through 4 with the hazard being greatest for the larger numbers. These ratings are listed for flammability, vapor irritation, and human toxicity.

Finally, the applicability of several potential control schemes is rated. These schemes are: (a) containment of the vapor through the application of foam or a water diffusion barrier, (b) reduction of vapor pressure and/or increase of viscosity through temperature reduction, and (c) prevention of vaporization through physical adsorption. The applicability of containment is separately rated for foam application and for use of a water diffusion barrier. The control scheme for physical adsorption was estimated from static dielectric constants of the chemicals as discussed earlier.

The temperature reduction approach to spill control has been evaluated for dry ice application and liquid nitrogen application. It is seen that nearly all the 200 volatile hazardous chemicals freeze at liquid nitrogen temperature (those chemicals for which freezing points could not be found in the literature were left blank), and in most cases the vapor pressure is reduced to insignificant values. It can be seen that, even at dry ice temperature, the vapor pressure of many of the chemicals considered is lowered sufficiently that the hazards associated with the vapor may be significantly reduced. It is for this reason that Battelle believes the temperature reduction approach has a very strong potential for control of volatile spills.

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LEGEND FOR TABLES 4 THROUGH 8

PHYSICAL PROPERTIES:
NA - Not Available
NL - Not Listed
NP - Not Pertinent
NF - Not Flammable

HAZARD RATINGS: The hazard is greater the larger the number, e.g., acetaldehyde (4) is more flammable than acetone (3).

CONTROL PROCEDURES

Containment:

N - The spill will not be contained with a foam, water, or film overlay because the ambient vapor pressure is too large

YF - The spill can be contained with a film or foam overlay

NW - The spill cannot be contained with a water overlay

MW - The spill may be contained with a water overlay

YW - The spill can be contained with a water overlay

Temperature Reduction:

F - Spill freezes at indicated temperature

neg - Vapor pressure is negligible at indicated temperature

$8x10^{-2}$ - Vapor pressure is $8x10^{-2}$ psi at indicated temperature

Adsorption:

VG - Very good; it is expected that this material will adsorb very well relative to the other chemicals

G - Good; it is expected that this material will adsorb well relative to the other chemicals

F - Fair; it is expected that this material will adsorb, but not well relative to the other chemicals

P - Poor; it is expected that this material will not adsorb especially well relative to the other chemicals

* Effectiveness of adsorption control procedures estimated by criteria other than the static dielectric constant.

Sources: Refs. 2, 7, 8, 9, 10, 11

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TABLE 4. REPRESENTATIVE HAZARDOUS HIGHLY VOLATILE CHEMICALS

(COMPOUNDS WITH BOILING POINTS OF 25°C OR LESS)

		Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
												Temp. Reduction		
No.	Chemical Name	Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel.Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	LN_2	CO_2	Adsorption
1.	Acetaldehyde (G)	20	19.0	1.5	-58	Yes	Ald	4	3	2	N	F 10^{-12}	$8x10^{-2}$	G
2.	Acetylene (G)	-84	Gas	0.9	Gas	No	-yne	4	1	-	N	F<10^{-4}	-	-
3.	Ammonia, anhydrous (G)	-33	Gas	0.6	NF	Yes	Base (amine)	1	4	2	N	F<10^{-9}	F 1 psi	F-G*
4.	Butadiene (G)	- 4	40	1.9	-105	No	-ene	4	1	1	N	F neg	.2	P*
5.	Butane (G)	0	55	2.0	-100	No	-	4	0	0	N	F neg	.2	P
6.	Butylene (G)	- 6	45	1.9	Gas	No	-ene	4	-	1	N	F neg	.3	P*
7.	Chlorine (G)	-31	100	-	NF	Yes	Cl	0	4	4	N	F<10^{-7}	1	P*
8.	Cyanogen chloride (G)	13	25	-	NF	No	CN, Cl	(Poisonous, Class A)			N	F neg	F.1	VG*
9.	Ethane (G)	-89	100	1.0	-211	No	-	Flammable	-	-	N	F $3x10^{-5}$	-	P*
10.	Ethyl chloride (G)	12	25.0	2.2	-45	No	Cl	2	-	1	YF, NW	F neg	.4	VG*
11.	Ethylene (G)	-104	1000	1.0	-213	Yes	-ene	4	0	1	N	F neg	-	P*
12.	Ethylene oxide (G)	11	27.0	1.5	0	Yes	Oxide	4	3	2	N	F	.5	G
13.	Fluorine (G)	-183	1000	-	NF	Reacts	F	0	-	4	N	-	-	P*
14.	Hydrogen chloride (G)	-85	100	-	NF	Yes	Acid, Cl	0	4	3	N	F-$2x10^{-5}$	-	G
15.	Hydrogen fluoride (G)	11	-	-	NF	-	Acid, F	0	4	4	N	F<10^{-10}	-	VG
16.	Hydrogen sulfide (G)	-60	100	1.2	Flammable Gas	Yes	S	4	-	3	N	F-10^{-6}	7	G*
17.	Isobutane (G)	-12	30	2.0	-117	No	-	Flammable	-	-	N	F neg	.4	P*
18.	Isobutylene (G)	- 7	27	-	-105 (cc)	No	-ene	4	-	1	N	F neg	.3	P*

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TABLE 4 (continued)

		Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
												Temp. Reduction		
No.	Chemical Name	Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel. Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	LN_2	CO_2	Adsorption
19.	Liquefied natural gas (G)	-161	100	-	Flammable gas	No	-	4	0	0	N	-	-	P*
20.	Liquefied petroleum gas (G)	- 40	100	-	-156 to -76	No	-	4	0	0	N	$<10^{-7}$	2	P*
21.	Methane (G)	-162	100	016	Flammable gas	No	-	4	0	0	N	F	-	P*
22.	Methyl bromide (G)	4	33	3.3	Practically NF	No	Br	1	3	4	YF, YW	F neg	.2	G*
23.	Methyl chloride (G)	-24	100	N.A.	32 (cc)	Sol	Cl	4	0	2	N	F neg	.7	G*
24.	Monochlorodifluoromethane (G)	-41	100	N.A.	NF	No	Cl, F	0	0	1	N	$F<10^{-7}$	2	-
25.	Nitrogen tetroxide (G)	21	20	N.A.	NF	Reacts	Acid	0	4	4	N	F neg	$F\ 7x10^{-2}$	P*
26.	Nitrosyl chloride (G)	-6	50	N.A.	NF	Reacts	Cl	0	-	-	N	F neg	F .3	VG*
27.	Phosgene (G)	8	2.8	-	NF	Reacts	Cl	0	-	4	N	F neg	.1	F*
28.	Propane (G)	-42	100	-	-156 (cc)	No	-	4	0	0	N	$F<10^{-7}$	-2	P*
29.	Propylene (G)	-48	100	1.5	-162 (cc)	No	-ene	4	0	1	N	F neg	.2	P
30.	Sulfur dioxide (G)	10	60	2.2	NF	Sol.	Acid	0	4	4	N	F neg	F .1	VG*
31.	Trichlorofluoromethane (G)	-81	17	3.6	NF	No	Cl, F		Not Listed		YF	F neg	$6x10^{-2}$	P*
32.	Trimethylamine (G)	3	3.3	2.0	NF	Yes	Amine	4	3	3	N	neg	.2	P*
33.	Vinyl chloride (G)	-14	15	2.2	-110	No	Cl, -ene	4	2	2	N	F neg	.4	F

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TABLE 5. REPRESENTATIVE HAZARDOUS VERY VOLATILE CHEMICALS

(COMPOUNDS WITH BOILING POINTS BETWEEN 25 AND 70°C)

		Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
No.	Chemical Name	Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel.Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	Temp. Reduction LN_2	Temp. Reduction CO_2	Adsorption
1.	Acetone (L)	56	4.9	2.0	4	Yes	Ketone	3	1	0	YF, NW	F neg	$1x10^{-2}$	G
2.	Acrolein (L)	52	5.0	1.9	-15	Yes	Ald.,-ene	3	3	3	YF, NW	F neg	$2x10^{-2}$	VG*
3.	Allyl chloride (L)	45	7.3	2.6	-20	No	-ene, Cl	3	3	3	YF, NW	F neg	$2x10^{-2}$	G*
4.	Bromine (L)	59	4.5	5.5	NF	No	Br	0	4	4	YF, NW	F neg	F 10^{-2}	P*
5.	Carbon disulfide (L)	45	7.3	2.6	-22	No	S	4	2	3	YF, YW	F neg	$2x10^{-2}$	P
6.	Chloroform (L)	61	4.0	-	NF	No	Cl	1	2	2	YF, YW	F neg	F 10^{-2}	F
7.	Dichlorodifluoromethane	30	NA	-	NF	No	Cl,F	0	0	1	N	$<10^{-7}$	1	P*
8.	Diethylamine (L)	56	0.4	2.5	5	Yes	Amine	3	3	2	YF	F neg	F 10^{-2}	P-F*
9.	Diethyl ether (L)	35	10.0	2.6	-40	Slight	-	4	1	2	YF	F neg	$4x10^{-2}$	F
10.	Dimethylamine (L)	69	3.3	1.6	20	Yes	Amine	4	2	2	YF	F neg	$7x10^{-3}$	F
11.	1,1-Dimethylhydrazine (L)	63	3.1	2.0	34	Yes	Amine	4	3	4	YF	F neg	F $7x10^{-3}$	-
12.	Ethyleneimine (L)	56	4.0	1.5	1	Yes	Amine	3	3	4	YF	-	$4x10^{-2}$	-
13.	Hexane (L)	69	3.3	3.0	-7	No	-	3	0	1	YF, NW	F neg	$6x10^{-3}$	P*
14.	1-Hexene (L)	64	4.0	3.0	-15	No	-ene	CFR:Combustible-liquid		-	YF, YW	F neg	$7x10^{-3}$	P*
15.	Hydrogen cyanide (L)	26	17	0.9	0 (cc)	Yes	CN	4	2	4	N	F 10^{-10}	F $5x10^{-2}$	VG
16.	Isohexane (L)	60	4.3	-	-20 (cc)	No	-	3	0	1	YF, NW	F neg	$1x10^{-2}$	P*
17.	Isopentane (L)	28	14	-	-70 (cc)	No	-	4	0	1	YF, NW	F neg	$6x10^{-2}$	P
18.	Isoprene (L)	34	11	2.4	-65 (cc)	No	-ene	4	1	1	YF, NW	F neg	$3x10^{-2}$	P

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TABLE 5 (continued)

No.	Chemical Name	Physical Properties: Boiling Point (°C)	Physical Properties: Vapor Pressure (PSIA/80°F)	Physical Properties: Rel. Vapor Density (Air=1)	Physical Properties: Flash Point (OC, °F)	Chemical Properties: Water Solubility	Chemical Properties: Functional Groups	Hazard Ratings: Flammability	Hazard Ratings: Vapor Irritation	Hazard Ratings: Poison	Control Procedures: Containment	Control Procedures: Temp. Reduction: LN_2	Control Procedures: Temp. Reduction: CO_2	Control Procedures: Adsorption
19.	Isopropyl ether (L)	69	-	3.5	-18	Slight	-	3	-	1	YF, NW	F neg	F $6x10^{-3}$	-
20.	Methyl acetate (L)	60	-	2.8	14	Sol.	Ester	3	-	1	YF, NW	F neg	$1x10^{-2}$	G*
21.	Methyl alcohol (L)	65	2.7	1.1	61	Yes	Alc.	3	1	2	YF, NW	F neg	$8x10^{-3}$	G*
22.	Methylene chloride (L) = Dichloromethane	40	90	2.9	NF	Slight	Cl	1	2	2	YF, YW	F neg	$3x10^{-2}$	F-G*
23.	Pentane (L)	36	1.0	2.5	-57 (cc)	No	-	4	0	1	YF, NW	F neg	$3x10^{-2}$	P
24.	1-Pentene (L)	30	12	2.4	0	No	-ene	Flammable			YF, NW	F neg	F $5x10^{-2}$	P
25.	Propionaldehyde (L)	48	6.5	2.0	-22	Slight	Ald.	3	2	2	YF	F neg	F $2x10^{-2}$	VG
26.	Propylene oxide (L)	34	11	2.0	-20	Sol.	Oxide	4	3	2	YF, NW	F neg	$3x10^{-2}$	-
27.	Sulfuryl chloride (L)	69	2.9	-	NF	Reacts	Cl	0	4	2	YF, NW	F neg	F $5x10^{-3}$	VG*
28.	Tetrahydrofuran (L)	66	2.3	2.5	-4	Sol.	Ether	3	1	2	YF, NW	F neg	$8x10^{-3}$	-
29.	Vinylidene chloride	32	12	3.4	0	No	Cl,-ene	3	2	3	YF	F neg	$4x10^{-2}$	-

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TABLE 6. REPRESENTATIVE HAZARDOUS VOLATILE CHEMICALS (COMPOUNDS WITH BOILING POINTS BETWEEN 70 AND 125°C)

		Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
												Temp. Reduction		
No.	Chemical Name	Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel. Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	LN_2	CO_2	Adsorption
1.	Acetic acid (L)	118	0.33	2.1	112	Yes	Acid	2	2	2	YF, NW	F neg	F 5×10^{-4}	G
2.	Acetonitrile (L)	82	1.8	1.4	42	Yes	Cyanide	3	1	3	YF, NW	F neg	F 3×10^{-3}	VG
3.	Acrylonitrile (L)	77	2.2	1.8	31	Yes	Cyanide, -ene	3	3	3	YF, NW	F neg	4×10^{-3}	VG
4.	Allyl alcohol (L)	97	0.54	2.0	90	Yes	Alc.,-ene	3	3	3	YF, NW	F neg	2×10^{-3}	F
5.	Benzene (L)	80	2.0	2.8	12 (cc)	No	-	3	1	3	YF, NW	F neg	F 3×10^{-3}	F
6.	Butyl alcohol (L)	118	0.15	2.6	97	Yes	Alc.	3	1	2	YF, NW	F neg	5×10^{-4}	G
7.	Butyl amine (L)	78	-	2.5	10	Yes	Amine	3	-	2	YF, NW	F neg	F 4×10^{-3}	-
8.	Butyraldehyde (L)	75	3.5	2.5	15	No	Ald.	3	2	2	YF, NW	F neg	4×10^{-3}	VG
9.	Carbon tetrachloride (L)	77	2.5	-	NF	No	Cl	0	2	4	YF, YW	F neg	F 4×10^{-3}	P
10.	Crotonaldehyde (L)	102	0.8	2.4	59	Slight	Ald.	3	3	3	YF, NW	F neg	F 1×10^{-3}	P
11.	Cyclohexane (L)	81	2.0	2.9	-4 (cc)	No	-	3	1	2	YF, NW	F neg	F 3×10^{-3}	P
12.	Dichloropropane (L)	96	1.1	3.9	70	No	Cl	3	1	3	YF, YW	F neg	F 2×10^{-3}	F-G*
13.	Dichloropropene (L)	77	2.7	3.8	95	No	Cl,-ene	3	2	3	YF, YW	F neg	F 4×10^{-3}	-
14.	Diisobutylene (L)	102	0.9	3.8	35	No	-ene	3	0	0	YF	neg	1×10^{-3}	P*
15.	Dioxane (L)	101	0.7	3.0	74	Yes	-	3	1	3	YF, NW	F neg	F 1×10^{-3}	P
16.	Dipentene (L)	81	-	4.7	113	No	-ene	2	-	0	YF	neg	10^{-2}	-
17.	Ethyl acetate (L)	77	1.9	3.0	55	Slight	Ester	3	1	2	YF, NW	F neg	4×10^{-3}	F
18.	Ethyl acrylate (L)	100	0.8	3.5	44	Slight	Ester,-ene	3	3	3	YF, NW	F neg	10^{-3}	-
19.	Ethyl alcohol (L)	78	1.2	1.6	64	Yes	Alc.	3	1	1	YF, NW	F neg	3×10^{-3}	G

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TABLE 6 (continued)

No.	Chemical Name	Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
		Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel.Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	Temp. Reduction		Adsorption
												LN_2	CO_2	
20.	Ethylene diamine (L)	117	0.3	2.1	150	Yes	Amine	3	3	3	YF, NW	F	F $5x10^{-4}$	F-P
21.	Ethylene dichloride (L)	84	1.6	3.4	60	No	Cl	3	2	3	YF, YW	–	$7x10^{-4}$	G
22.	Ethylene glycol dimethyl ether (L)	85	1.4	-	34	Slight	-	Flammable		-	YF, NW	–	$2x10^{-3}$	-
23.	Formic acid (L)	101	0.85	1.6	138	Yes	Acid	2	3	3	YF, NW	F neg	F $1x10^{-3}$	VG
24.	Heptane	98	0.9	3.5	250(cc)	No	-	3	0	1	YF, NW	F neg	$1x10^{-3}$	P
25.	1-Heptene (L)	94	1.3	3.4	25(cc)	No	-ene	3	1	0	YF, NW	F neg	F $7x10^{-4}$	P
26.	Hydrogen peroxide	125	0.15	-	NF	Yes	-	0	2	1	YF, NW	neg	$3x10^{-4}$	-
27.	Isopropyl alcohol (L)	82	0.9	2.1	65	Yes	Alc.	3	1	2	YF, NW	F neg	$3x10^{-3}$	G*
28.	JP-3 (L)	30 to 160	4.7	-	110-150	No	-	3	1	1	YF, NW	F neg	$<4x10^{-2}$	P*
29.	Methyl acrylate (L)	81	0.8	2.6	44	Slight	-ene	3	3	3	YF, NW	F neg	$3x10^{-3}$	-
30.	Methyl ethyl ketone (MEK) (L)	80	1.8	2.5	22	Sol.	Ketone	3	1	2	YF, NW	F neg	$3x10^{-3}$	G*
31.	Methyl isobutyl ketone (L)	116	0.42	3.5	75	Slight	Ketone	3	1	1	YF, NW	F neg	$5x10^{-4}$	G*
32.	Methyl methacrylate (L)	101	0.85	3.6	50	Slight	-ene	3	3	3	YF, NW	F neg	$1x10^{-3}$	-
33.	Nitric acid (L)	89	1.7	NA	NF	Sol.	Acid	0	3	3	YF, NW	F neg	$2x10^{-3}$	-
34.	Nitromethane (L)	101	0.7	2.1	110	Slight	-	3	-	1	YF, NW	F neg	F $1x10^{-3}$	VG
35.	1-Octene (L)	121	0.037	3.9	70	No	-ene	Flammable			YF, NW	F neg	$4x10^{-4}$	P*
36.	Perchloroethylene (L) = Tetrachloroethylene	121	0.4	-	NF	No	-ene, Cl	0	1	2	YF, YW	F neg	F $4x10^{-4}$	P

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TABLE 6 (continued)

No.	Chemical Name	Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
		Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel.Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	Temp. Reduction		Adsorption
												LN_2	CO_2	
37.	Petroleum ether (L)	94-140 F	NA	-	0	No	--	4	-	1	MF	F neg	$<6\times10^{-2}$	-
38.	Phosphorous oxychloride (L)	107	NP	5.3	NF	Decomposes	Cl, P	0	4	4	YF, NW	F neg	F 8×10^{-4}	-
39.	Phosphorous trichloride (L)	76	2.6	4.7	NF	Decomposes	Cl, P	3	-	0	YF, NW	F neg	NO 4×10^{-3}	P*
40.	n-Propyl acetate (L)	102	0.7	3.5	65	Slight	Ester	3	1	2	YF, NW	F neg	1×10^{-3}	F
41.	n-Propyl alcohol (L)	97	0.36	2.1	81	Sol.	Alc.	3	1	2	YF, NW	F neg	2×10^{-3}	G
42.	Propylene dichloride (L) = Dichloropropane	96	1.1	3.9	70	No	Cl	3	1	3	YF, YW	neg	1×10^{-3}	G
43.	Pyridine (L)	115	0.43	2.7	68	Sol.	Amine	3	2	1	YF, NW	F neg	F 5×10^{-4}	-
44.	Tetramethyl lead (L)	110	-	9.2	-	No	Pb	-	-	-	YF, YW	-	-	-
45.	Toluene (L)	111	0.6	3.1	55	No	-	3	1	2	YF, NW	F neg	7×10^{-4}	-
46.	Trichloroethane (L)	74	1.6	4.6	NA	No	Cl	1	1	2	YF, YW	F neg	F 4×10^{-3}	F
47.	Trichloroethylene (L)	87	1.5	4.5	90(cc)**	No	Cl, -ene	1	1	2	YF, YW	F neg	F 2×10^{-3}	-
48.	Valeraldehyde (L)	103	0.7	3.0	54	No	Ald.	3	1	2	YF, NW	F neg	10^{-3}	-
49.	Vinyl acetate (L)	73	1.4	3.0	23	Slight	Ester, -ene	3	1	2	YF	F neg	F 5×10^{-3}	-

** Practically nonflammable.

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TABLE 7. REPRESENTATIVE HAZARDOUS CHEMICALS WITH INTERMEDIATE VOLATILITY

(COMPOUNDS WITH BOILING POINTS BETWEEN 125 AND 200°C)

		Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
												Temp. Reduction		
No.	Chemical Name	Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel. Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	LN_2	CO_2	Adsorption
1.	Acetic anhydride (L)	139	0.13	3.5	136	Yes	Anhydride	2	3	3	YF, NW	F neg	F 2×10^{-4}	G
2.	Acrylic acid (L)	141	0.12	2.5	118	Yes	Acid,-ene	2	3	2	YF, NW	F neg	F 2×10^{-4}	-
3.	Amyl acetate (L)	146	0.13	4.5	91(cc)	Slight	Ester	3	-	1	YF, NW	neg	1×10^{-4}	-
4.	Amyl alcohol (L)	138	0.09	3.0	77(cc)	Slight	Alcohol	3	1	2	YF, NW	neg	2×10^{-4}	G*
5.	Aniline (L)	184	0.008	3.2	168	Slight	Amine	1	1	3	YF, MW	neg	2×10^{-5}	F
6.	Benzaldehyde (L)	179	0.017	3.7	165	No	--	2	-	2	YF, MW	neg	2×10^{-5}	G
7.	Benzoyl chloride (L)	197	NA	4.9	162	Decomposes	Cl	1	4	2	YF, NW	F neg	F 1×10^{-5}	G
8.	Benzyl chloride (L)	179	NA	4.4	153	No	Cl	2	-	2	YF, YW	F neg	F 2×10^{-5}	-
9.	Butyl acetate	126	0.28	4.0	88	Slight	Ester	3	1	2	YF, NW	neg	4×10^{-4}	F
10.	Butyl acrylate (L)	149	0.12	4.4	118	No	Ester,-ene	2	1	1	YF, NW	neg	1×10^{-4}	-
11.	Butyric acid (L)	164	-	3.0	161	Yes	Acid	2	-	2	YF, NW	F neg	F 5×10^{-3}	P
12.	Chlorobenzene (L)	132	0.28	3.9	97	No	Cl	3	0	2	YF, YW	F neg	F 3×10^{-4}	F
13.	Cresols (L)	177	0.018	3.7	180	No	Phenol	1	2	2	YF, YW	F neg	F 3×10^{-5}	G
14.	Cumene (L)	152	0.33	4.1	111(cc)	No	--	2	1	1	YF, NW	F neg	9×10^{-5}	-
15.	Cyclohexanone (L)	156	0.5	3.4	129	Slight	Ketone	2	3	1	YF, NW	F neg	F 6×10^{-5}	G
16.	Cyclohexyl alcohol (L)	161	0.07	3.5	160	Slight	Alc.	1	1	1	YF	neg	3×10^{-5}	G
17.	1-Decene (L)	171	0.04	4.8	128	No	-ene	-	-	-	YF	F neg	F 2×10^{-5}	P*
18.	Dichlorobenzene (L)	181	0.035	5.1	165	No	Cl	1	2	1	YF, YW	F neg	F 2×10^{-5}	F-G
19.	Dicyclopentadiene (L)	170	0.09	-	90	No	-ene	3	1	2	YF	F neg	F 3×10^{-5}	-
20.	Diethylcarbonate (L)	127	0.23	4.1	115	No	Ester	3	-	2	YF	F neg	F 3×10^{-4}	P
21.	Diethyl glycol dimethyl ether (L)	162	0.06	-	158	Yes	--	-	-	-	YF	neg	5×10^{-5}	-

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TABLE 7 (continued)

		Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
												Temp. Reduction		
No.	Chemical Name	Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel. Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	LN_2	CO_2	Adsorption
22.	Diisobutyl ketone (L)	168	4.9	-	140	No	Ketone	2	-	1	YF	neg	$4x10^{-5}$	G*
23.	Dimethyl sulfate (L)	189	0.017	4.4	240	Slight	$-SO_4$	1	4	4	YF, MW	F neg	F $1x10^{-5}$	-
24.	Dodecene (L)	190	0.005	5.8	134	No	-ene	2	1	1	YF, NW	F neg	F $1x10^{-5}$	P
25.	Ethylbenzene (L)	136	0.2	0.9	80	No	-	3	2	2	YF, NW	F neg	$7x10^{-5}$	P
26.	Ethyl butanol (L)	146	0.03	3.5	128	No	Alc.	-	-	-	YF, NW	F neg	10^{-4}	G*
27.	Ethylene dibromide (L)	131	0.27	-	NF	No	Br	0	1	3	YF, YW	F neg	F $3x10^{-4}$	F
28.	Ethylene glycol (L)	198	0.002	-	240	Yes	Alc.	1	0	1	YF, NW	F neg	F $7x10^{-6}$	G*
29.	2-Ethylexylacrylate (L)	130	-	-	180	No	-ene	2	2	-	YF, NW	neg	$3x10^{-4}$	-
30.	Furfural (L)	162	0.05	3.3	153	Slight	Ald.	2	2	3	YF, MW	F neg	F $5x10^{-5}$	VG
31.	Furfuryl alcohol (L)	171	-	3.4	167	-	Alc.	2	-	1	YF, NW	F neg	$3x10^{-5}$	G*
32.	Gasolines (L)													
	Automotive (4.23 gm lead/gal)	199	NA	-	-36(cc)	No	-	3	1	2	YF, NW	F neg	$5x10^{-6}$	P*
	Aviation (4.86 gm lead/gal)	171	NA	3.4	50(cc)	No	-	3	1	2		F neg	$3x10^{-5}$	P*
33.	Glutaraldehyde (L)	188	NA	3.4	NA	Yes	Ald.	-	-	-	YF, NW	F neg	F $1x10^{-5}$	G*
34.	Heptanol (L)	176	0.01	4.0	160	No	Alc.	-	-	-	YF, NW	F neg	F $7x10^{-5}$	G*
35.	Hexanol (L)	157	0.5	3.5	149	Slight	Alc.	CFR:Combustible liquid	-	-	YF, NW	F neg	$<3x10^{-5}$	P*
36.	JP-4 (L)	176 to 287	1.8	-	-10 to +40(cc)	No	-	3	1	1	YF, NW	F neg	$<3x10^{-5}$	P*
37.	JP-5 (L)	176 to 287	NA	-	140(cc)	No	-	1-2	-	1	YF, NW	F neg	F $3x10^{-4}$	-
38.	Mesityl oxide (L)	130	-	3.4	87	Slight	-	3	-	3	YF, NW	F neg	$<6x10^{-5}$	P*
39.	Mineral spirits (L)	154 to 202	0.07	3.9	105-140 (cc)	No	-	2	-	0	-	-	-	-

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TABLE 7 (continued)

		Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
												Temp. Reduction		
No.	Chemical Name	Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel. Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	LN_2	CO_2	Adsorption
40.	Monomethanolamine (L) = ethanolamine	170	0.01	2.1	200	Sol	amine,alc.	1	2	2	YF, NW	F neg	F $4x10^{-5}$	G
41.	Morpholine (L)	128	0.32	3.0	100	Sol	amine	3	1	1	YF, NW	F neg	$3x10^{-4}$	F
42.	Nonane (L)	151	-	4.4	88	No	-	3	-	0	YF,NW	F neg	F $9x10^{-5}$	P
43.	Nonene (L)	140	0.12	-	78	No	-ene	3	1	0	YF, NW	F neg	$1x10^{-4}$	P*
44.	Octanol (L)	195	0.002	4.5	178(cc)	No	alc.	2	-	1	YF, NW	F neg	F $9x10^{-6}$	G
45.	Phenol (S)	182	0.016	3.2	185	Yes	phenol	1	2	3	YF, NW	F neg	F $2x10^{-5}$	F-G
46.	Phosphorous pentachloride (S)	162 (Sub)	NA	7.2	NF	NA	Cl, P	NA	NA	NA	-	F	F	-
47.	β-Propiolactone (L)	155	NA	2.5	165	Sol.	ester	2	-	0	YF, NW	F neg	$5x10^{-5}$	-
48.	Propionic acid (L)	141	0.09	2.5	134	Sol.	acid	2	2	2	YF, NW	F neg	F $1x10^{-4}$	P-F
49.	Propionic anhydride (L)	169	-	4.5	165	Decomposes	acidic	2	-	2	YF, NW	F neg	$3x10^{-5}$	-
50.	Propylene glycol (L)	187	0.002	-	225	Sol.	alc.	1	0	0	YF, NW	neg	$1x10^{-5}$	G
51.	Styrene (L)	145	0.14	3.6	93	No	-ene	3	2	2	YF, NW	F neg	10^{-4}	P
52.	Sulfur monochloride (L)	138	0.3	4.7	266	Reacts	Cl	1	4	4	YF, NW	F neg	F $2x10^{-4}$	-
53.	Turpentine (L)	155	0.15	-	95	No	-	3	1	1	YF, NW	neg	$6x10^{-5}$	-
54.	1-Undecene (L)	193	0.01	5.3	160	No	-ene	NL	NL	NL	YF, NW	F neg	10^{-5}	-
55.	Vinyl toluene = Methyl styrene (L)	168	103	4.1	137	No	-ene	2	2	1	YF, NW	F neg	$4x10^{-5}$	P
56.	Xylenes (L)	132 to 144	0.16	3.7	75 to 84	No	-	3	1	2	YF, NW	F neg	F<$3x10^{-4}$	P

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TABLE 8. REPRESENTATIVE HAZARDOUS CHEMICALS WITH LOW VOLATILITY (COMPOUNDS WITH BOILING POINTS ABOVE 200°C) AND MISCELLANEOUS COMPOUNDS

		Physical Properties				Chemical Properties		Hazard Ratings			Control Procedures			
No.	Chemical Name	Boiling Point (°C)	Vapor Pressure (PSIA/80°F)	Rel. Vapor Density (Air=1)	Flash Point (OC, °F)	Water Solubility	Functional Groups	Flammability	Vapor Irritation	Poison	Containment	Temp. Reduction LN_2	Temp. Reduction CO_2	Adsorption
1.	Acetone cyanohydrin (L)	Decomposes	0.009	2.9	165(cc)	Yes	Cyanide	1	1	4	YF, NW	F neg	F	VC*
2.	Acetophenone (L)	202	NA	4.1	180	No	Ketone	2	-	1	YF, MW	F neg	F $7x10^{-6}$	G
3.	Adiponitrile (L)	290	NA	3.7	199	No	Cyanide	1	1	3	YF, NW	neg	$4x10^{-8}$	VC*
4.	Ammonium hydroxide (L)	NP	NA	NP	NF	Yes	Base (amine)	-	-	-	YF, NW	F neg	F	-
5.	Chlorohydrins (L)	NP	0.16	-	92	Slight	Cl	3	3	4	YF	-	-	-
6.	n-Decyl alcohols (L)	230	0.0001	5.5	180	No	Alc.	1	0	0	YF	F neg	F 10^{-6}	G*
7.	Dibutyl phthalate (L)	335	NA	NA	355	No	Ester	1	0	0	YF, MW	F neg	F neg	-
8.	Diethanolamine (L)	268	NA	-	305	Yes	Amine	1	2	2	YF, NW	F neg	F $2x10^{-7}$	-
9.	Diethylene glycol (L)	245	-	-	255	Yes	Alc.	1	0	1	YF, NW	F neg	F $7x10^{-7}$	G*
10.	Diethylenetriamine (L)	207	0.01	-	210	Yes	Amine	1	2	2	YF	neg	$5x10^{-6}$	-
11.	Ethylene cyanohydrin (L)	230	0.001	-	265	Yes	CN, Alc.	1	0	2	YF	-	$1x10^{-6}$	VC*
12.	2-Ethylhexyl alcohol (L)	365	0.006	4.4	185	Slight	Alc.	1	1	1	YF, NW	-	neg	G*
13.	Formaldehyde solution (L)	NP	0.04	1.0	182(cc)	Yes	Ald.	2	3	3	YF, NW	F	-	VC*
14.	Hexamethylenediamine (L)	202	0.004	NA	160	Yes	Amine	1	1	3	YF, MW	F neg	F $5x10^{-6}$	P
15.	Hexamethylenetetramine (S)	NP	NP	NA	482	Yes	Amine	-	-	-	YF, NW	F neg	F	-
16.	JP-1 (kerosene) (L)	260	.05	-	100(cc)	No	-	2	1	1	YF, NW	F neg	neg	P*
17.	Kerosene (L)	200 to 260	.05	-	100(cc)	No	-	2	1	1	YF, NW	F neg	<$6x10^{-6}$	-
18.	Naphthalene (S)	218	NA	4.4	190	No	-	1	2	2	YF, YW	F neg	F $3x10^{-6}$	P
19.	Nonanol (L)	213	NA	5.0	210	No	Alc.	1	0	0	YF, NW	F neg	F $3x10^{-6}$	G*
20.	Nonylphenol (L)	304	NA	-	300	Slight	Phenol	1	1	1	YF, NW	F neg	$3x10^{-8}$	-
21.	Oleum (L)	Decomposes	NP	-	NF	Sol.	Acid	0	4	3	YF, NW	-	-	-

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TABLE 8 (continued)

No.	Chemical Name	Physical Properties: Boiling Point (°C)	Physical Properties: Vapor Pressure (PSIA/80°F)	Physical Properties: Rel. Vapor Density (Air=1)	Physical Properties: Flash Point (OC, °F)	Chemical Properties: Water Solubility	Chemical Properties: Functional Groups	Hazard Ratings: Flammability	Hazard Ratings: Vapor Irritation	Hazard Ratings: Poison	Control Procedures: Containment	Control Procedures: Temp. Reduction LN_2	Control Procedures: Temp. Reduction CO_2	Control Procedures: Adsorption
22.	Paraformaldehyde (S)	Decomposes	NP	-	199	Slight	Ald.	- - - Not Listed - - - -			YF	F	F	F*
23.	Phosphorus pentasulfide (S)	514	NP	-	Flammable	Reacts	P	1	-	2	YF, NW	F neg	F neg	-
24.	Tall oil (L)	NA	NA	-	NA	NA	-	NA	NA	NA	-	-	-	P*
25.	Tetradecanol (L)	263	NA	74	285	No	Alc.	1	-	0	YF, NW	F neg	F $3x10^{-7}$	G*
26.	1-Tetradecene (L)	251	NA	6.8	230(cc)	No	-ene	1	-	0	YF, NW	F neg	F $5x10^{-7}$	P*
27.	Tetrahydronaphthalene (L)	208	0.012	4.6	190	No	-	1	1	2	YF, NW	F neg	F $4x10^{-6}$	-
28.	Toluene 2,4-diisocyanate (L)	250	.001	6.2	270	No	-	1	3	4	YF	F neg	$8x10^{-7}$	-
29.	Trichlorobenzene (L)	213	-	6.3	210	Decomposes	Cl	-	-	-	YF, YW	F neg	F neg	F-P
30.	Tridecene (L)	233	.001	-	175	No	-ene	- - - Not Listed - - -			YF, NW	F neg	$2x10^{-6}$	P*
31.	Tridecyl alcohol (L) = Tridecanol	274	NA	6.9	250	No	Alc.	1	0	0	YF, NW	F neg	F $2x10^{-7}$	G*
32.	Triethanolamine (L)	Decomposes	NA	5.2	375	Sol.	Amine	1	0	1	YF, NW	F neg	F $7x10^{-2}$	-
33.	Triethylenetetramine (L)	277	NA	5.0	290	Yes	Amine	1	2	1	YF	F neg	$2x10^{-7}$	-

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SECTION 6

PROPOSED VOLATILE SPILL SUPPRESSION CONCEPTS

In Section 4, current field methods for controlling the volatilization from landborne spills of hazardous materials were discussed. The conclusions of Section 4 were that vapor source removal, water flooding, and controlled ignition were effective means of vapor control, when circumstances were favorable. Section 5 presented a brief technical discussion of the liquid vaporization process and an analysis of a simple model for vaporization from a spill. It was determined that temperature reduction, sorption, and vapor barriers were three possible means by which the spill vaporization rate could be controlled. This section discusses possible alternative approaches to the application of promising vapor control techniques. The concepts described herein were devised from existing technology in other areas of engineering.

There are basic issues not explicitly addressed in these concepts, including:

1. Personnel Safety -- Most of the systems described allow for personnel to be at some distance from the spilled material, thus decreasing their exposure risks. The use of safety equipment by personnel who may be exposed to hazardous materials is certainly recommended, but it was not within the scope of this program to examine personnel safety per se.

2. Availability -- The problem of equipment availability will always exist in a resource-limited world. Battelle did not study the distribution of equipment needed across the U.S., since the goal of this program was to examine technology, not economics.

3. Time -- The concepts presented cover a range of time scales required for application, from several hours (for CO_2 application) to several days (energy transfer concepts).

4. Equipment Loss -- When dealing with spills of hazardous materials, the equipment used should be considered expendable. If the spill does present a hazard, the attitude of spill control personnel is that the sacrifice of equipment is a better choice than the sacrifice of humans. For this reason, Battelle did not examine the effects of corrosion, etc., on the conceptual equipment.

Table 9 contains a list of the plausible control methods, many of which were generated in idea sessions. The methods have been organized under major headings or concepts which emphasize the similarities in the overall approach. The table also serves as a general outline for this section.

TABLE 9. CONCEPTUAL TECHNOLOGIES

DIKING/EARTHMOVING CONCEPTS

a. Manual Construction of Dikes and Ditches
b. Earthmoving Equipment (Bulldozers, etc.) for Construction of Dikes or Trench-Digging
c. Standard Earthmoving, Agricultural, or Specially Constructed Plows to Mix the Hazardous Chemicals With the Underlying Soil
d. Remote-Control or Wire-Guided Systems to Construct Dikes or Dig Trenches
e. Oil Booms as Dikes
f. Foam Barriers as Dikes
g. Explosives to Form Dikes

PREFORMED COVERS DEPLOYMENT CONCEPTS

a. Parachutes as Preformed Covers for Spills
b. Deployment of Blankets or Tarpaulins on the Spill by Means of Parachutes
c. Spring-Loaded Tarpaulins That Would Unfold on Landing in the Spills
d. Tarpaulins or Blankets Deployed While Falling by Means of Rockets
e. Deployment of Parachutes in an Upside-Down Fashion by Means of Helicopter Downwash
f. Cannon Arrangement to Fire a Folded Cover, Weighted Along its Edges in Such a Manner That it Would Rotate in Flight and Centrifugally Deploy to its Full Size
g. Drag Parachutes or Tarpaulins Over the Spill Either Manually or with Manipulators or Cranes
h. Fire Navy Line Guns Over the Spill to Provide a Means of Pulling a Tarpaulin or Cover Across a Spill
i. Tarpaulin Deployment by Fixing One Side to the Ground and Dragging it Over the Spill by Means of Rockets or Helicopters
j. Parachutes or Tarpaulin Placement Over Spills While Directing Air Blasts Under or Over the Parachutes or Tarpaulins to Levitate Them
k. Geodesic Dome Constructed Over the Spill
l. Inflate a Balloon Over the Spill

(continued)

TABLE 9 (continued)

SKIN-TYPE COVERS DEPLOYMENT CONCEPTS

a. Spray Chemicals That Would Polymerize and Form Covers on the Spill
b. Spray Foam Onto the Spill
c. Form a Cover (e.g., Nylon) at the Site
d. Preformed Film Overlay System

LARGE OBJECT DELIVERY CONCEPTS

a. Manual Deployment
b. Catapult to Deliver Large Objects Into the Spill
c. Four-Bar Linkage to Deliver Large Objects
d. Air Cannon to Deliver Large Objects
e. Explosive Cannon to Deliver Large Objects
f. Portable Conveyor to Deliver Large Objects
g. Helicopter or Airplane to Drop Large Objects Onto a Spill
h. Device Similar to an Agricultural Bale Thrower to Deliver Large Objects to Spills
i. Earthmoving Equipment for Dumping Large Objects on a Spill

SMALL OBJECT DELIVERY CONCEPTS

a. Standard Straw or Silage Blower to Disperse Small Objects
b. Small-Scale Blower Modeled After a Straw or Silage Blower (with Less Range and a Smaller Delivery Rate)
c. Air Cannon Delivery of a Quantity of Small Objects or Particles Contained in a Canister Which Will Release the Objects at a Certain Distance or Time
d. Explosive Cannon Delivery of a Quantity of Small Objects or Particles Contained in a Canister Which Will Release the Objects at a Certain Distance or Time
e. Catapult Delivery of a Quantity of Small Objects or Particles Contained in a Canister Which Will Release the Objects at a Certain Distance or Time
f. Conventional Crop Dusting Airplanes to Dispense Small Objects or Particles
g. Dispersal of Small Objects with a Centrifugal Pump
h. Dispersal of Small Objects or Particles with a Sandblasting-Type Pump Arrangement

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TABLE 9 (continued)

i. Dispersal of Small Objects or Particles With a Centrifugal Slinger Similar to the Type Used on Sanding Trucks

SLURRY TRANSFER CONCEPTS

a. A Standard Hydro-Seeder to Disperse a Slurry

b. Use of "Slippery Water" Component in the Slurry to Increase the Spray Range of Conventional Water-Hose-Based Pumping Systems

c. Utilize Existing Fire Truck Pumps and Hoses to Pump Slurries

d. Deploy a Slurry Transfer Hose Over the Spill with a Long Boom, Either a Crane or a Specially Constructed Boom

LIQUID TRANSFER CONCEPTS

a. Pumps and Liquids From Available Fire Trucks for Pumping Liquids

b. Slippery Water to Extend the Range of Conventional Water-Based Pumping Systems

c. Deployment of a Liquid-Dispensing Hose Nozzle with a Balloon

d. Deployment of a Hose and Nozzle with a Supporting Boom, Either a Commercial Crane or with a Specially Constructed Boom

ENERGY TRANSFER CONCEPTS

a. Flame-Throwers to Heat or Ignite a Spill

b. Infrared Lights with Parabolic Reflectors to Heat a Spill

c. Solar Energy Lenses to Increase the Temperature of the Chemical Spill

d. Sonic Disturbance or Blast

e. Increase the Temperature of the Spill Via a Standard Heat Exchanger System

f. Microwave Transmitters

g. Incendiary Bombs to Increase the Temperature of the Spill

h. Decrease the Temperature of the Spill Via Standard Cooling Equipment

i. Air Curtain Destructor Devices Used to Burn the Hazardous Chemical in a Controlled Situation

DIKING/EARTHMOVING CONCEPTS

One of the more effective techniques for controlling volatilization is to capture the spilled material in pools and pump it into closed containers. Since spills will generally spread over a wide area, tools to alter the contour of the terrain would be useful for spill containment. As an alternative to capture, burying the spill in the soil is also effective in decreasing the vaporization rate.

Manual Construction of Dikes and Ditches

This operation is a simple and common-sense treatment for the less dangerous spills. Workers would dike the spill or dig drainage ditches with shovels in order to contain the spill. Their tools might possibly be made of metals or of plastics which would reduce the risk of causing sparks when hitting obstructions.

It is estimated that the development of a set of prototype tools would cost approximately $20,000 over a period of four months.* Protective gear for the exposed workers would be necessary.

Earthmoving Equipment (Bulldozers, etc.) for Dike and Trench Forming

Earthmoving equipment could be used to construct dikes or dig trenches. The equipment's blades could be fabricated of a metal or plastic which would reduce the sparking hazard. The engines could be equipped with spark-arresting mufflers. The use of diesel engines (compared to gasoline engines) is recommended because of their lower operating temperatures. The operator's cab should be fitted with an auxiliary breathing system such as is presently used by fire and rescue squads.

A representative vehicle is the Caterpillar D8K crawler tractor shown in Figure 2. Equipped with a stock bulldozer blade and adjustable ripper, this machine costs $160,000. It is estimated that the total cost for a model modified as described above would be $200,000.

Spill Burial or Mixture With Underlying Soil

Standard earthmoving or agricultural rippers, plows, discs, or harrows might be used to bury the hazardous chemical mixtures within the underlying soil. The working depth for such tools may range from about 4 in. for the case of an agricultural harrow to 72 in. for the case of a single shank ripper mounted on a large crawler tractor.

The blades of such devices could be fitted with wearing surfaces made of nonsparking materials, such as beryllium copper, to replace the stock steel parts. This would give safer operation during spill coverage operations.

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* Each cost estimate for a prototype system was calculated by obtaining five independent cost estimates from experienced researchers, eliminating the highest and lowest estimate, and averaging the remaining three estimates (rounded to the nearest $1000).

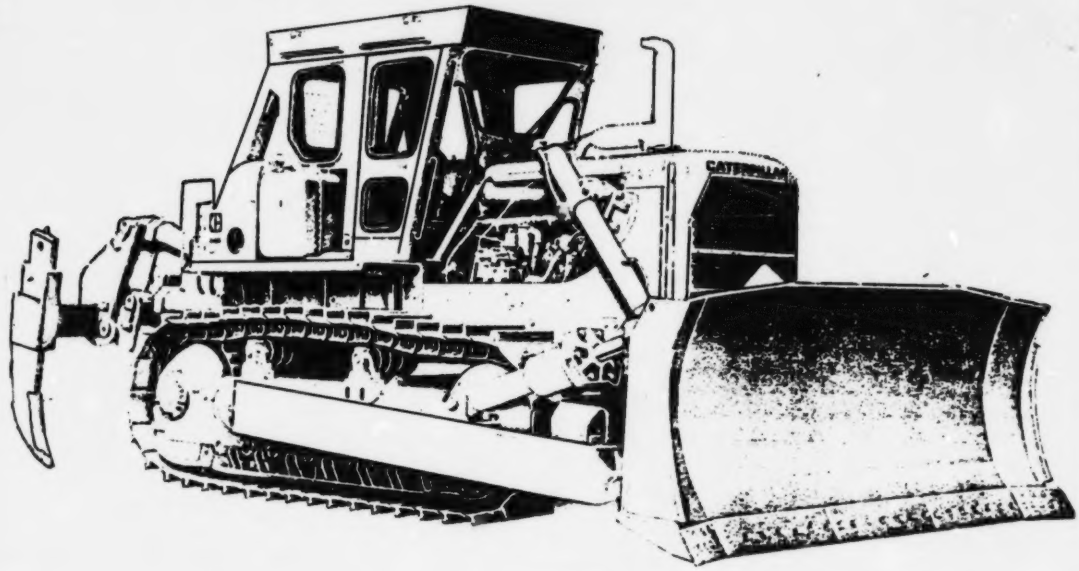

Figure 2. Caterpillar D8K crawler tractor.
(Source: Caterpillar advertisement)

The cost of a typical 11-ft-wide harrow is $2600.* The cost of a 40-hp diesel tractor required to pull such a harrow is $8200. The price of a large ripper-mounted crawler is $160,000.

Remote-Control or Wire-Guided Systems

Because of possible hazards of a toxic or explosive atmosphere at a spill site, it may be desirable to operate diking or trenching equipment by remote control. This would obviously lessen the risk to the equipment operator.

In the last several years the remote control of increasingly larger and more complex equipment has been achieved. The objective has been to remove the operator from a hostile environment, while still retaining most of the machine's performance. A typical system is shown in Figure 3, which is a remote-controlled Bobcat excavator.

It is estimated that a crawler such as the Caterpillar D8K could be purchased and fitted with a Moog radio control for a total cost of $260,000.

Oil Booms as Dikes

A number of firms have developed inflatable booms for containing oil spills on waterways. Such booms could be used at land spill sites. Water might be used instead of air to inflate the booms in order to form a sturdier barrier and to help conform to terrain irregularities.

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* Available commercial equipment is currently described in English units of measurement; where applicable, this practice will be followed in this report.

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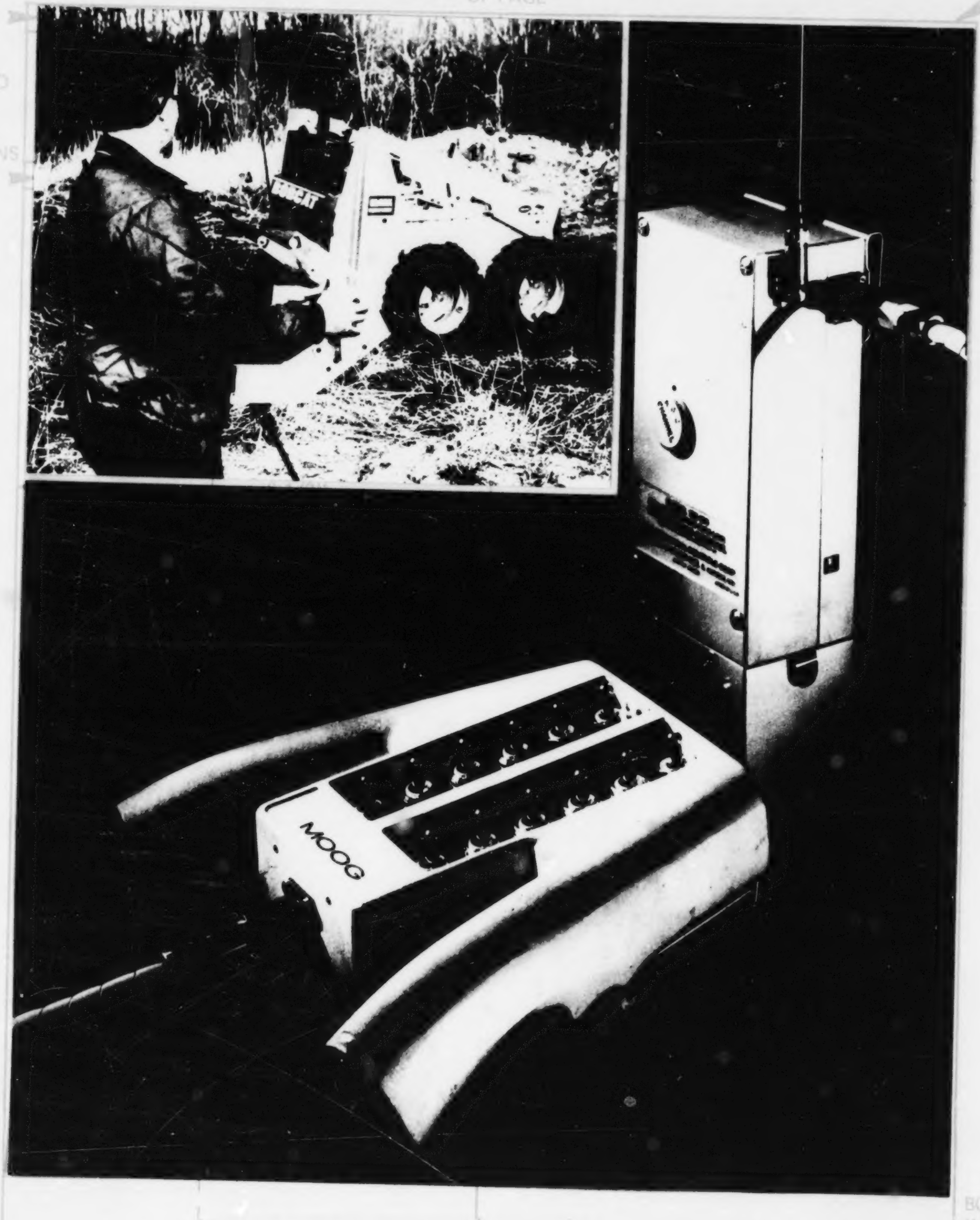

Figure 3. Remote-controlled Bobcat excavator.
(Reproduced by permission from SAE)

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A typical oil boom is made up of sections of inflatable rubber bladders. The bladders may also be filled with water. A section of oil boom is typically 50 ft long.

Foam Barriers as Dikes

A foam dispenser might be used to quickly erect a barrier around a pollution source as depicted in Figure 4. The foam would rapidly stiffen and form a barrier or dike which would contain the spill.

A stock Hydro-Seeder* might be used as-is or be modified to suit this purpose. The cost of such a unit with a 3000-gal capacity is approximately $12,000.

Explosives to Form Dikes

An explosive charge might be used under certain conditions to form a dike to contain the spill. This would be possible when nearby personnel and structures would not be affected by the consequences of the blast. The barrier erected by the charge would not be impervious, but would slow the spread and hence the evaporation of the spill.

PRE-FORMED COVERS DEPLOYMENT CONCEPTS

In this group, and in the group that follows, the principal concept involves the placement of a vapor barrier over the spill so as to reduce volatility and introduction of the hazardous vapors into the atmosphere.

These concepts are viewed as rapid response techniques, since air delivery to even the most remote areas can occur quickly. Rapid setup of the covers is also envisioned.

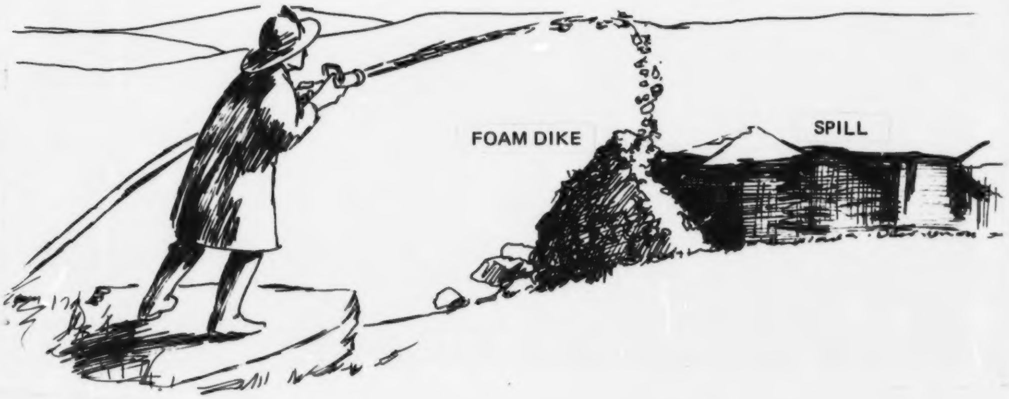

Figure 4. Foam dike deployment concept.

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* Trade name, Bowie Industries, Inc.

Parachutes as Spill Covers

Parachutes could be dropped directly onto the pollution source to serve as covers.

Parachutes used as pollution covers may have several disadvantages. Stock parachutes are made of thin nylon material with about one-third of the weight used in denim jeans. The value of this fabric as a pollution cover is questionable. The use of heavier nonporous fabrics may be possible, but air vents would probably need to be provided in the canopy for proper air flow during descent, thus degrading the covering ability of the parachute when in position. Parachutes need to fall at a rate of about 20 ft/sec to form properly. When the parachute's canopy tends to collapse as the tension goes out of the lines, which are suspended from the canopy, the uniform shape of the canopy disappears and the canopy may land somewhat unpredictably and in a relatively small heap.

Parachutes are seldom built in diameters over 100 ft. Such parachutes require a 3000-lb ballast weight to form properly. The cost for an ordinary 100-ft-diameter nylon parachute is typically about $300.

Blankets or Tarpaulins Deployed by Parachutes

Blankets or tarpaulins could be dropped on the spill by means of parachutes. While delivery could be made in remote locations in an expeditious manner, it would probably be necessary to at least partially spread out the tarpaulins after landing, either manually or by means of devices such as grapple hooks, or by spring-loaded mechanisms contained in the tarpaulin package.

A typical 20-ft x 20-ft chemical-resistant tarpaulin will cost about $400 and weigh about 35 lbs. A suitable parachute would probably be about 16 ft in diameter and cost about $800.

Spring-Loaded Covers

Tarpaulins could be designed to unfold automatically after being dropped or thrown onto the spill, as shown in Figure 5. A typical scheme would use steel springs fastened diagonally across the tarpaulin. The springs would unfold the tarpaulin when a series of restraining straps or bands for holding the package together were released. Similar schemes have been used successfully for the compact storage and deployment of underwater nets.

A typical prototype chemical-resistance, spring-loaded 20-ft x 20-ft tarpaulin would cost about $8000 to develop and $1000 to produce in quantity.

Rocket Deployment of Falling Covers

A tarpaulin or blanket could be dropped from a height and deployed by means of rockets while falling.

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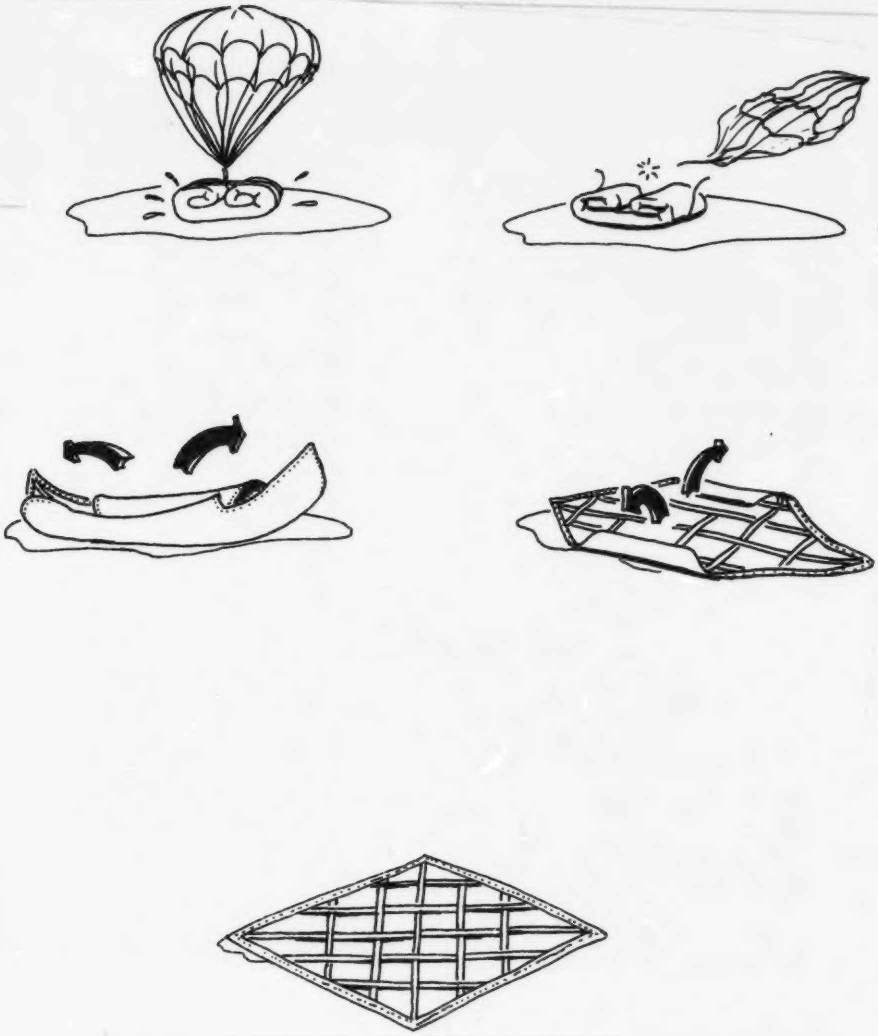

Figure 5. Spring-loaded tarpaulin deployment concept.

Inasmuch as this concept is rather novel, it would not be easy to transfer existing technology to make it workable. Significant problems to be solved would include the identification of the most expeditious way of using rockets to open the tarpaulin or cover, the point of descent at which the rockets are to be fired, the avoidance of fire hazards due to the use of rockets near volatile spills, and a means of ensuring that the tarpaulin or blanket would be deployed in a safe and predictable manner.

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Spill-Cover Deployment by Helicopter Downwash

Parachutes might be deployed in an upside-down fashion by means of a helicopter's downwash. The downwash would serve to open the parachute and maintain its shape. An air velocity on the order of 20 ft/sec would be required to deploy a conventional parachute. A full-size parachute for a UH-1 helicopter would be about 100 ft in diameter and would be suspended about 200 ft below the helicopter, as shown in Figure 6.

As stated previously, conventional parachutes are made of thin nylon material, which might not be effective for covering spills. If a special parachute were designed for this purpose, vent holes would probably need to be cut in the canopy to allow air to be bled through for proper inflation of the canopy.

A suitably-sized parachute of this type would cost approximately $6000.

Spill-Cover Deployment by Special Cannon

A folded cover fired from a cannon may present several problems. The desired range of such a system would probably not exceed 500 ft. There are no known commercially available cannon arrangements suitable for use with this concept. The most applicable mortar currently in the inventory of the U.S. Army, the 4.2-in., has a minimum effective range of 2750 ft. The problem is therefore to develop both a folded cover assembly that deploys in flight and a special launcher for it. Two of the more promising concepts might be based upon a pneumatic cannon used in circus stunts or an impulse-rocket such as the U.S. Army's M72 Light Anti-Tank Weapon. The folded cover could be weighted along its edges and ejected from the cannon in such a manner that it would rotate in flight and centrifugally deploy to its full size.

Development costs for a prototype system have been estimated at approximately $200,000 over a period of 12 months.

Manual and Mechanical Manipulator Deployment of Spill Covers

Parachutes or tarpaulins that have been placed near the spill could be dragged across the spill either manually or by using devices such as cranes. It might be desirable to attach a simple claw at the end of a hydraulic crane mast in order to place the tarpaulin in position.

A typical 35-ton-capacity hydraulic crane has a horizontal reach of 150 ft and sells for approximately $170,000. A simple manipulator claw could be added to the boom for approximately $20,000.

Spill-Cover Deployment With Navy Line Guns

A line gun could be used to throw lines across the spill which would enable a tarpaulin or cover to be pulled across the spill. The U.S. Navy and Coast Guard use line guns in naval operations. There are small commercial versions also available, which can throw lines distances of about 300 ft, as shown in Figure 7.

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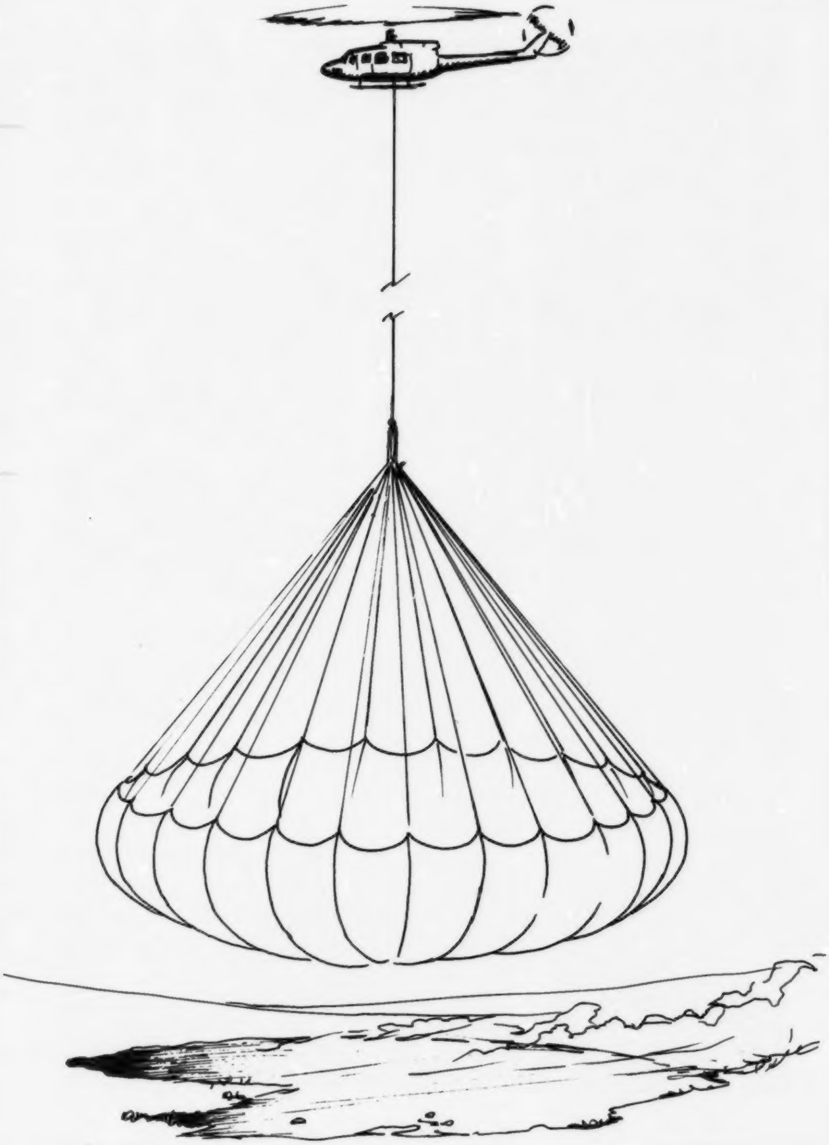

Figure 6. Upside-down parachute deployment concept.

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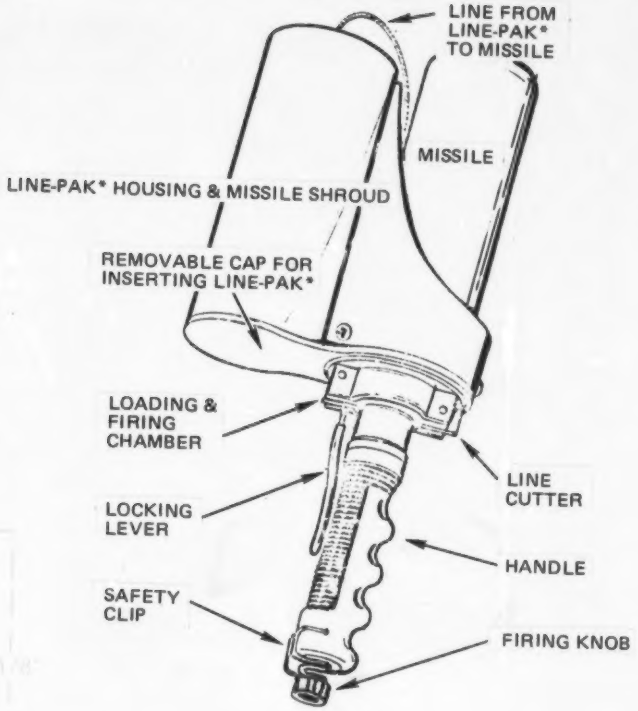

Figure 7. Commercial line-throwing gun.

Such small line guns cost about $300.

Spill Cover Deployment by Rocket or Helicopter

A tarpaulin could be placed in position over the spill by means of helicopters or rockets. One side of the tarpaulin would be fastened to the ground along one side of the spill to stabilize it during positioning. Once in place, helicopters or rockets would be used to drag the tarpaulin over the spill. The use of helicopters is probably the more practical approach since they would probably be more controllable and stable in positioning the tarpaulin than rockets would be. Contact with commercial fireworks manufacturers indicates that suitable rockets would need to be specially developed for such a task. It is not known to what extent a developmental program for such a task would need to be pursued.

Since helicopters are normally in the inventory of local and state authorities, the major cost for this system would be only for that of a suitable tarpaulin. The cost is typically $800 for a 20-ft^2 chemically-resistant tarpaulin.

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Use of Air Blasts to Aid in Deployment of Spill Covers

Parachutes or tarpaulins could be dragged into position with the help of air blasts directed over or underneath them in order to levitate them, as shown in Figure 8. Tarpaulins equipped with pull ropes would be required, along with fans to levitate the tarpaulins. If four 40,000-cfm fans, each powered by a 120-hp diesel engine, are required, the total cost of the system would be about $85,000.

Spill Containment by Structural Enclosure

A geodesic dome or similar prefabricated building might be erected over a spill. A commonly available 22-ft x 60-ft inflatable plastic greenhouse is available. It consists of plastic sheeting placed over a supporting framework. The cost of this simple enclosure is about $2500.

Inflatable Spill Cover

A balloon-like structure could be inflated over a spill. An inflatable plastic cover measuring 22 ft x 60 ft is available from commercial sources. It requires a small air blower running continuously to keep it inflated and costs about $2500.

SKIN-TYPE COVERS DEPLOYMENT CONCEPTS

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Skin-type covers consist of a thin layer or sheet of relatively nonporous material that can be placed over or formed on top of the spill to reduce volatility. These concepts are probably in the intermediate time range, upwards of one day after the spill.

In-Situ Formation of Polymer Film

A spraying system could be devised to deliver a polymerizing film-forming cover over the spill. A likely candidate for such a spraying system is the Hydro-Mulcher* system which has been used for functions as diverse as mulching, tree seeding, as demonstrated in Figure 9, and flame-throwing. It can deliver up to 3000 gal of liquid at a range of up to 200 ft in about 20 minutes.

A 3000-gal stock Hydro-Mulcher system suitable for mounting on a truck would cost about $12,000.

Spill Coverage by Foam

Foam could be sprayed directly onto the spill. It would need to be cohesive and light enough to form a solid layer on top of the spill. In addition, the foam would need to be capable of resisting permeation by the spill vapor over a period of time.

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* Trade name, Bowie Industries, Inc.

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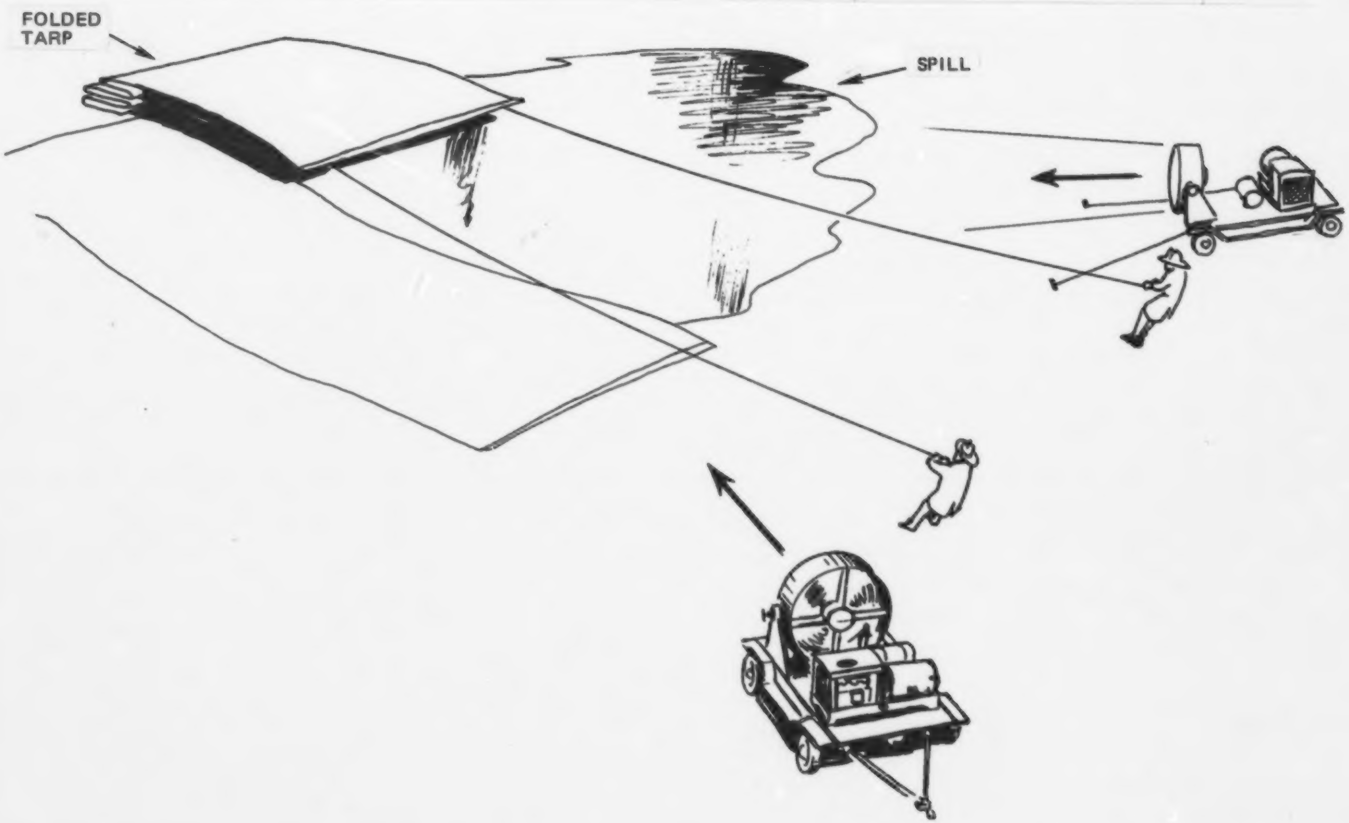

Figure 8. Levitating tarpaulin concept.

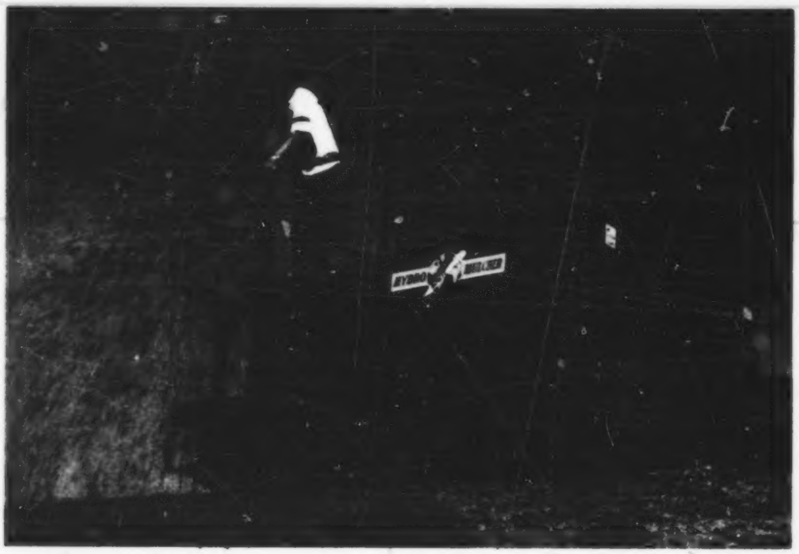

Figure 9. Commercial Hydro-Mulcher.

(Source: Advertisement)

A typical foam-spraying apparatus, the Bliss Jet-X-2 system, can deliver up to 15,000 gal of water-based foam per minute and requires 42 gpm of water at 100 psi. The unit weighs 50 lbs and is 22 in. x 22 in. x 34 in. A Bliss Jet-X-2 system costs approximately $630.

On-Site Spill Cover Formation

A cover could be formed at the site of the spill. The most expeditious method of doing this would probably be to form the cover directly over the spill. A similar system has been developed for the stabilization of silt on lake and ocean beds at diver work sites, as shown in Figure 10. A similar but longer system suitable for deployment by a telescoping crane or similar device, as shown in Figure 11, could probably be developed for about $100,000.

Use of Preformed Films

A spool of preformed film could be unrolled over a spill area by a suitable mechanical device. A typical deployment scheme might involve use of a standard earthmoving backhoe modified to accept rolls of preformed film similar to that shown in Figure 12.

A prototype system could be developed in about 8 months at a cost of approximately $75,000.

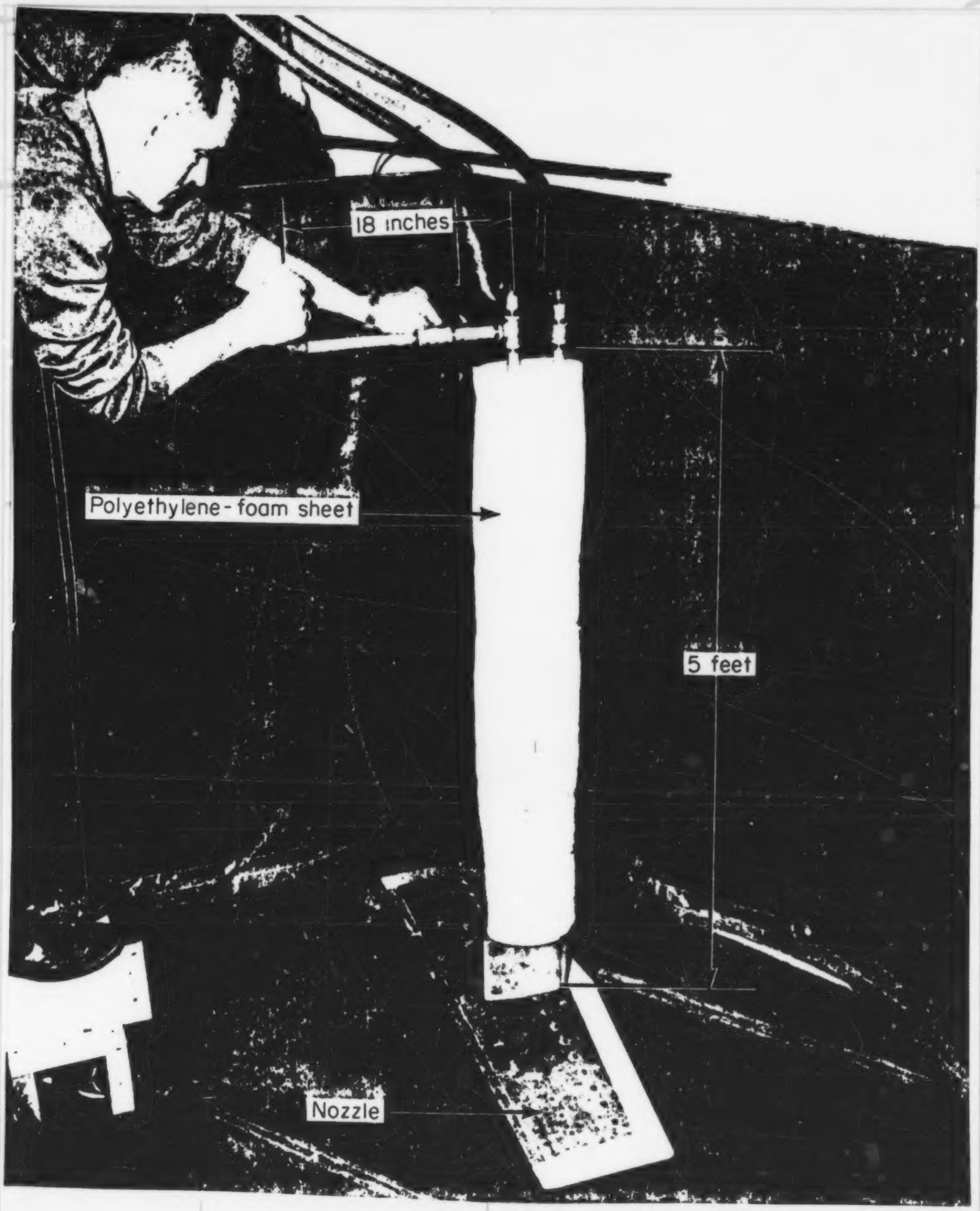

Figure 10. Silt stabilization polymer applicator.
(Source: Battelle)

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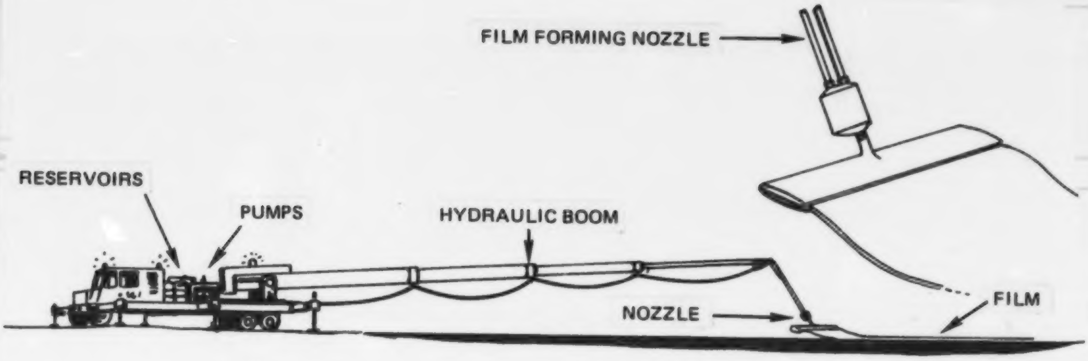

Figure 11. Conceptual technique for forming and deploying a cover over the spill.

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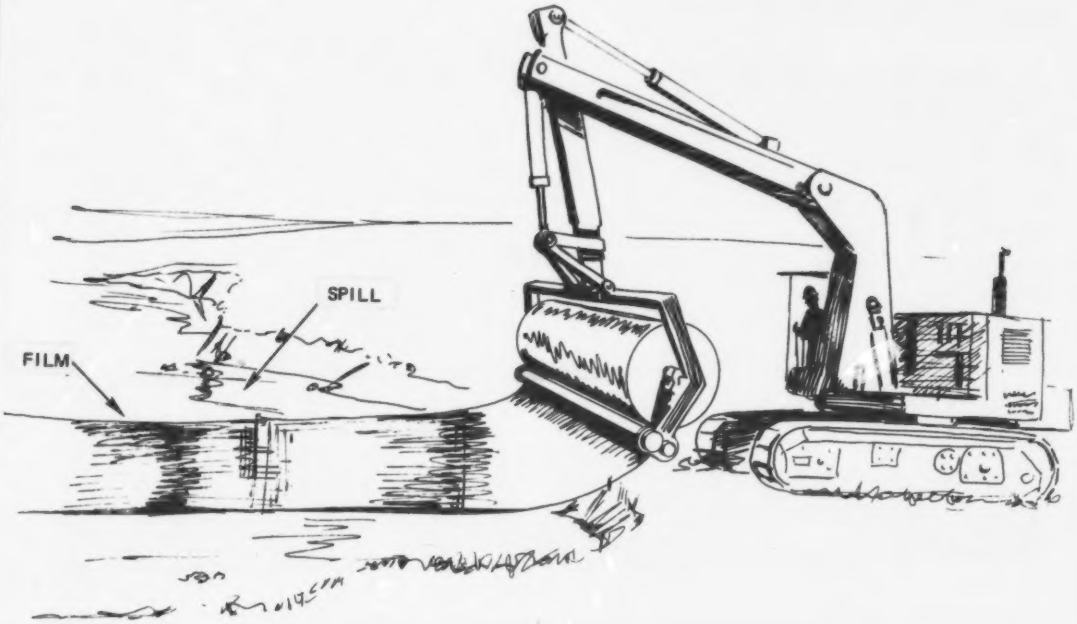

Figure 12. Deployment of a preformed film.

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LARGE OBJECT DELIVERY CONCEPTS

One of the more promising vaporization control concepts is that of spill temperature reduction. The temperature reduction could be accomplished by adding liquid nitrogen or dry ice to the spill.

Dry ice is commercially available in 50-lb blocks. It is desirable to examine means to safely emplace these blocks in the spilled material. Other forms of dry ice frequently commercially available are 5-lb disks and pellets. Dry ice production facilities can be found in almost every city.

Similarly, bales of straw (80 lb each) and bags of charcoal (25 lb) could be lofted into the spill as sorbents.

Manual Deployment

A large object such as a cake of dry ice could be simply thrown into the spill manually. However, the object would have to be safe for manual handling and be of manageable size and weight. It is also assumed that it would be safe for the individual to get close enough to the spill to deliver the object.

Since there should be personnel at the spill site, the cost of this concept would be minimal.

Catapult Devices

A catapult could be used to deliver large objects into spills. Catapults are typically used at shooting ranges for hurling skeet targets. Typical targets weigh about 1 lb.

An investigation did not find a longer, more suitable catapult. A compressed-gas-powered catapult, as shown in Figure 13, could probably be developed for large object delivery. Spring-powered catapults could also be developed. The developmental costs for a prototype system have been estimated to be approximately $58,000 over a period of 6 months.

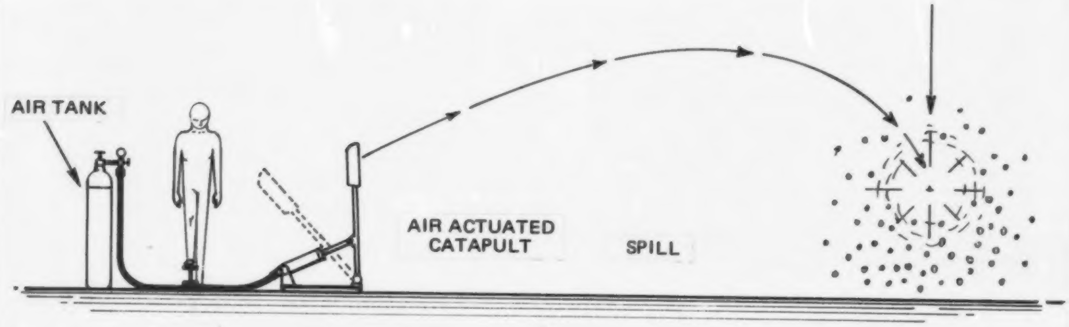

Figure 13. Catapult delivery concept.

Four-Bar Linkage Devices

A mechanism using a four-bar linkage arrangement could be used for continuous delivery of moderately large objects into spills. Figure 14 shows how the four-bar linkage could be arranged for significant ranges. Investigation has shown that such four-bar linkage mechanisms are not generally commercially available.

A prototype system could be developed in about 6 months at a cost of approximately $53,000.

Air Cannon Devices

An air cannon could be used to deliver large objects onto spills. Air cannons are not generally available on the commercial market. The same principle was used in World War I for short-range mortars and is occasionally used today in "human cannonball" acts at circuses.

Developmental costs for a prototype system have been estimated at approximately $73,000 over a period of 8 months.

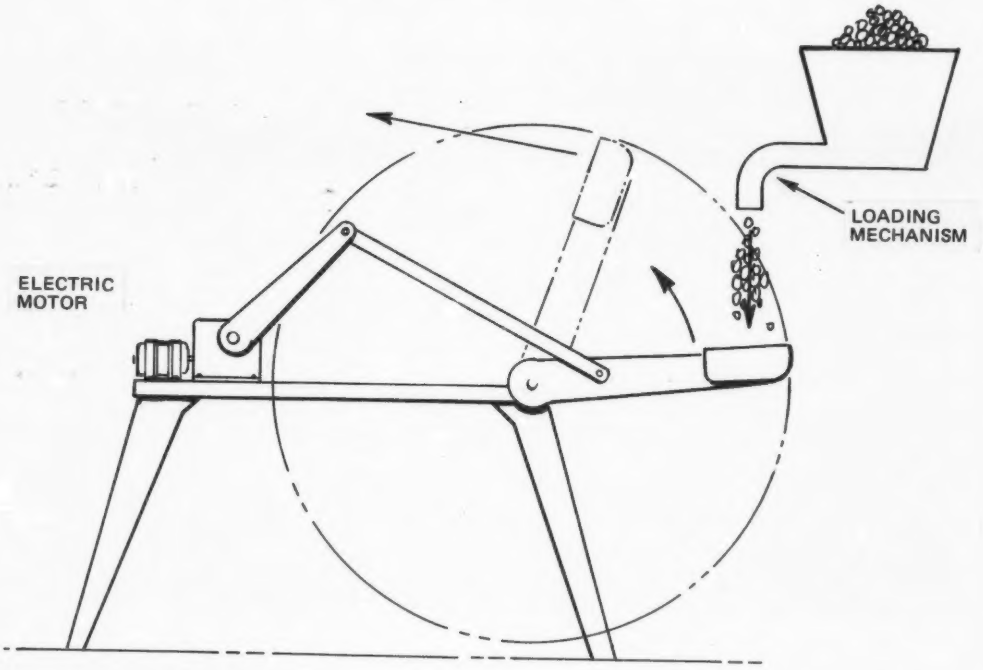

Figure 14. Four-bar linkage concept.

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Explosive Cannon Devices

An explosive cannon could be used to deliver large objects onto spills. The largest mortar generally used by the U.S. Army has a 4.2-in. bore. Similarly, the largest cannon has a 175-mm (6.9-in.) bore. It is doubtful that these bore sizes are large enough to warrant a serious consideration for this proposed use. Both of these weapons normally are used at ranges of several miles.

A prototype short-range explosive cannon for firing large objects could probably be developed in about 8 months at a cost of approximately $97,000.

Portable Conveyors

A portable conveyor, similar to agricultural or industrial types used to transport grain, crushed rock, or hay bales, could be used to deliver large objects into spills. A typical 56-ft conveyor can have a reach of 35 ft beyond its towing wheels and be self-propelled.

Typical cost for such a unit is $11,000.

Helicopters or Airplanes

Large objects could be dropped on spills by means of helicopters or airplanes. Helicopters or airplanes would probably be available to pollution authorities. The UH-1 "Huey" Iroquois helicopter, in the inventory of many National Guard units, has a payload capability of 4000 lb. A helicopter could carry onboard a dumpable container full of large objects that could be dropped onto the spill.

Developmental costs for a prototype system attachable to the helicopter have been estimated at approximately $48,000 over a period of 6 months.

Devices Similar to Agricultural Bale-Throwers

A device similar to a bale-thrower, used on agricultural hay balers to throw hay bales onto wagons, could be used to hurl large objects onto chemical spills (Figure 15). A stack bale thrower can toss 80-lb hay bales a distance of 20 ft or more. A similar device could be developed for increased range.

A stack bale-thrower costs $1100. Some modifications would be required for mounting it on a skid or truck bed.

Earthmoving Equipment

Large objects could be dropped on spills by using earthmoving equipment. A number of earthmoving machines might be used for this purpose. Probably the best choice would be a wheel loader. Such a machine could travel into spills and dump its load where desired. It should be suitably equipped with a spark-arresting muffler, tires than can withstand contact with the spilled liquid, and an operator life support system (Figure 16).

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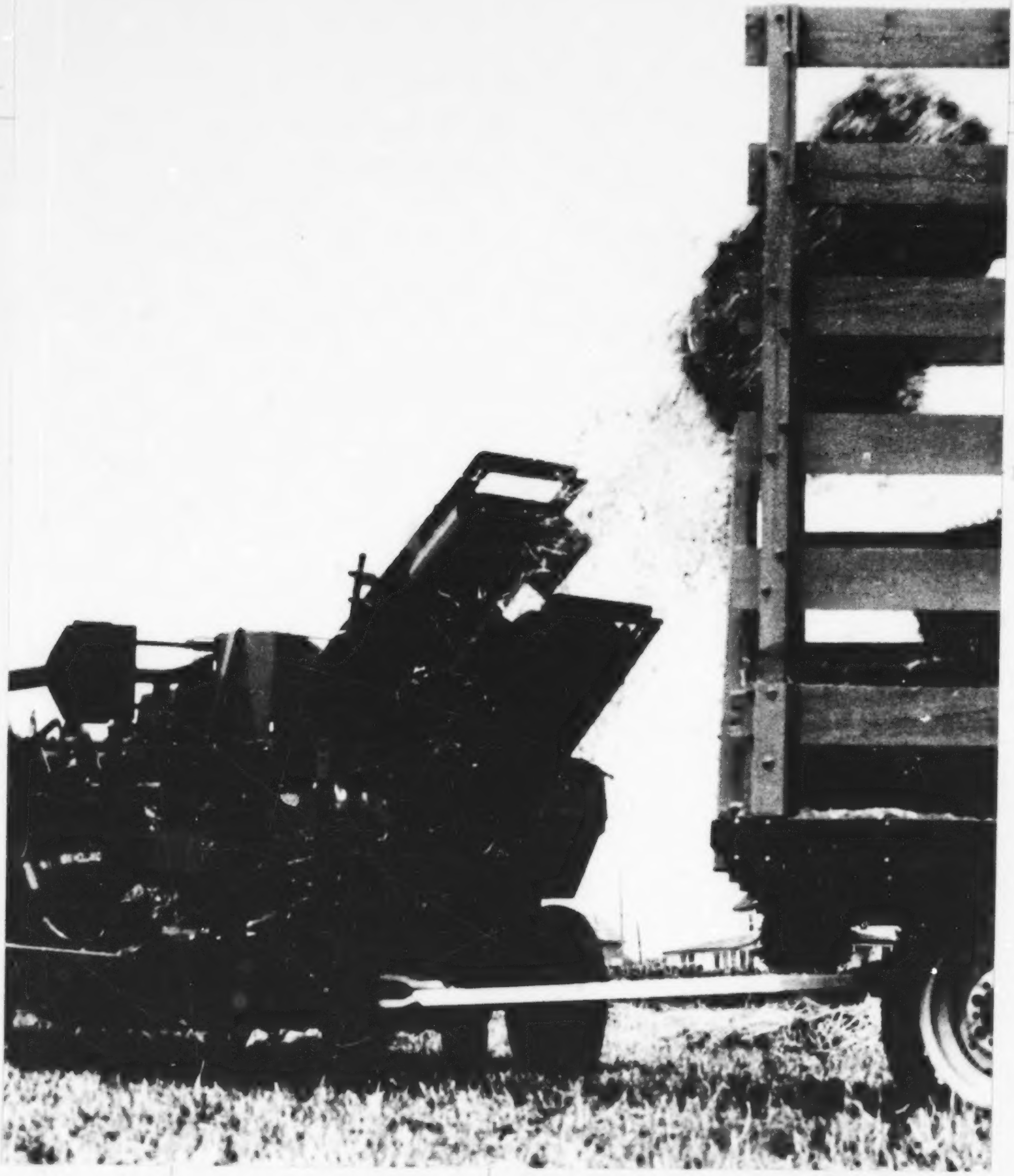

Figure 15. Commercial stack bale-thrower.
(Source: Advertisement)

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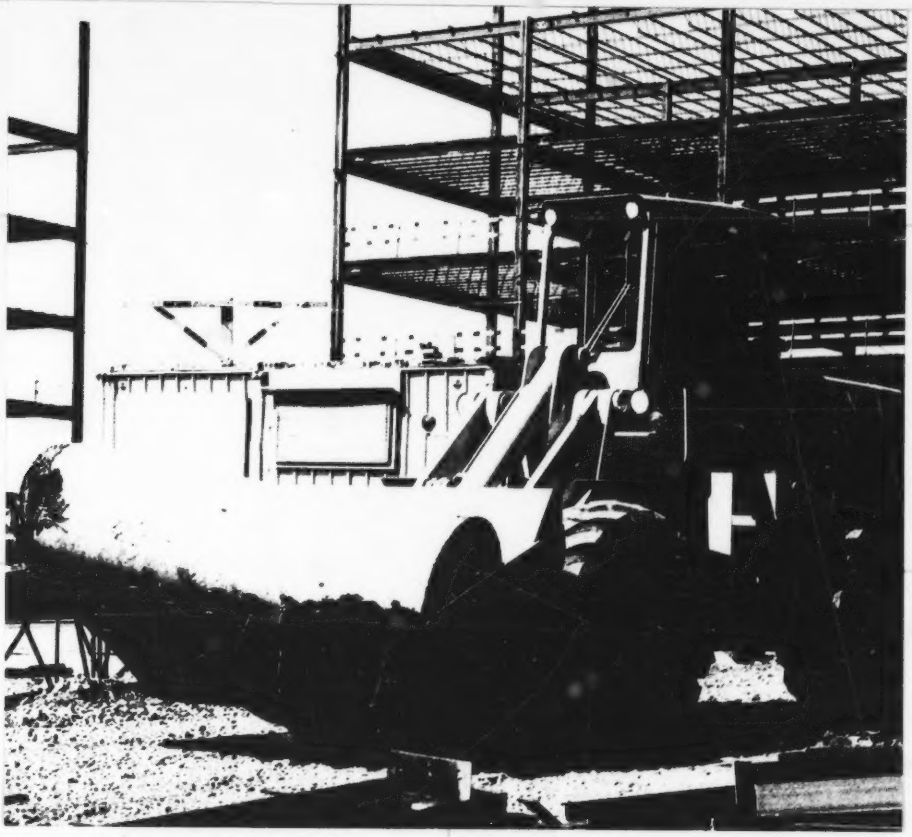

Figure 16. Commercial wheel loader.
Source: Advertisement)

The price of a typical wheel loader with a 2.5-yd^3 (23,000-lb) capacity bucket is about $60,000.

SMALL OBJECT DELIVERY CONCEPTS

These concepts were defined for use in spreading dry ice pellets, sand, straw, charcoal, and other small items onto the spill.

Standard Straw or Silage Blowers

A centrifugal fan, such as a forage blower used for filling agricultural silos, could be used to disperse small objects onto spills. A typical large-capacity agricultural forage blower can blow material at rates up to 150 tons/hr (5000 lb/min). Particle velocities would approach 130 ft/s. Relatively dense particles could probably travel 100 or 200 ft from the blower's outlet (Figure 17).

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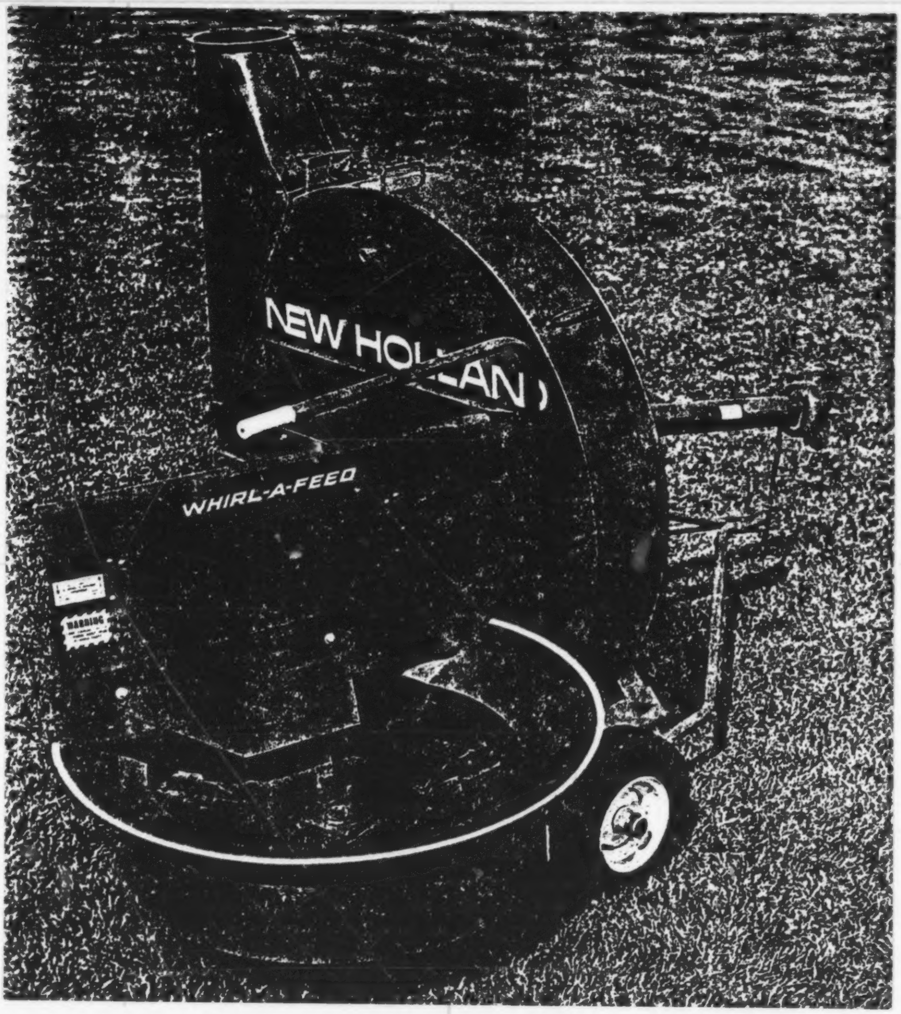

Figure 17. Commercial forage blower.
(Source: Advertisement)

The cost for a typical blower would be $1500. A base for it and a stationary diesel engine to power it would cost approximately $10,000. The total cost would be about $11,500.

Small-Scale Blowers

A small-scale version of a forage blower may be a feasible method of distributing small objects over a spill.

A small stock blower or fan might be modified for use as a material handling blower. However, such units will probably need to be constructed more

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sturdily than blowers or fans which move only air. A power source such as a small air-cooled diesel engine would also be required.

Such a system could probably be developed in about 6 months at a cost of about $40,000, if a suitable stock blower can be found.

Air Cannon - Disintegrating Canisters

An air cannon could be used to propel a disintegrating canister full of small objects over a spill. The small objects would be distributed over the spill as the canister disintegrated.

Neither the air cannon nor the canisters are commercially available. The canister to be used would need to be compatible with the cannon. It is doubtful that any standard military ammunition would be suitable for use in an air cannon.

A prototype system could be developed in about 9 months at a cost of approximately $100,000.

Explosive Cannon - Disintegrating Canister

An explosive cannon could fire a disintegrating canister full of small objects over a spill. The small objects would be distributed over the spill as the canister disintegrated.

The major problems with this approach are that cannons in the U.S. Army typically have bores no larger than 175 mm (6.9 inches) and they are usually weapons designed for ranges of several miles, rather than several hundred feet. These problems might limit the particle-carrying capacity of special ammunition and could cause aiming and deployment problems.

Developmental costs for a prototype system have been estimated at approximately $115,000 over a period of 9 months.

Catapult - Disintegrating Canister

A gas-oven oil accumulator could hurl a canister containing a quantity of small objects over a spill. The small objects would then be distributed over the spill as the canister disintegrated.

The major problem with this approach is that neither suitably-sized catapults nor canisters are commercially available. Both components would have to be designed and built to order.

A prototype system could be developed in about 9 months at a cost of approximately $80,000.

Crop-Dusting Airplanes

Conventional crop-dusting airplanes could be used to disperse small objects or particles over spills. Typical crop-dusting airplanes have delivery

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payloads between 100 and 2000 lb, depending on the size of the airplane. Their range from their point of origin is on the order of 40 mi.

Crop-dusting airplanes typically charge $75 for a 25-acre dusting job.

Centrifugal Pumps

Small objects could be spread over a spill with a centrifugal pump. This concept might be attempted with the particles either wet or dry. In the case of wet particles, the pump would be handling a slurry, which is a standard industrial practice. For dry particles, the pump would act essentially as a centrifugal slinger. Provisions would have to be made for feeding the dry particles into the eye of the impeller. The particles exiting from the periphery of the impeller would tend to impinge upon any diffusers that might be in the vicinity of the impeller and would tend to either shatter and/or lose velocity.

The concept could probably be attempted with existing centrifugal pumps on emergency equipment that is presently available.

Sandblasting-Type Pump Arrangement

A commercially available sandblaster might be used to strew small particles over a spill area. A typical commercial sandblaster can deliver particles up to 1/8-in. diameter at rates up to 1500 lb/hr (Figure 18).

Such a sandblaster is typically mounted on a truck bed and costs about $20,000.

Centrifugal Sanders

Small objects or particles could be spread over spills using highway centrifugal sanders. Typical centrifugal sanders are mounted on the rear of dump truck boxes. They consist of an auger mounted transversely across the rear of the dump box, which feeds sand to a centrifugal slinger. The entire mechanism can be hydraulically driven. A typical spreader assembly suitable for mounting on an 8-ft-long dump truck box has a capacity of 4.5 yd^3, which can be unloaded in about 10 minutes and scattered 20 ft (Figure 19).

Such a unit typically costs $5000.

SLURRY TRANSFER CONCEPTS

The concepts considered here were devised for the transfer of slurries, such as lime/water, solid/liquid nitrogen, or rapid-setting inorganic foams, to the spill.

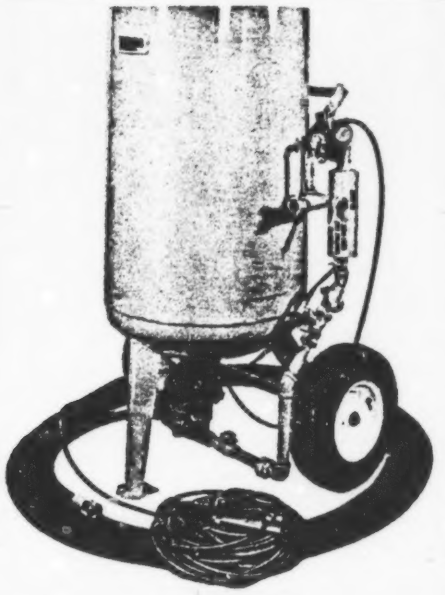

Figure 18. Commercial sand-blasting equipment.
(Source: Advertisement)

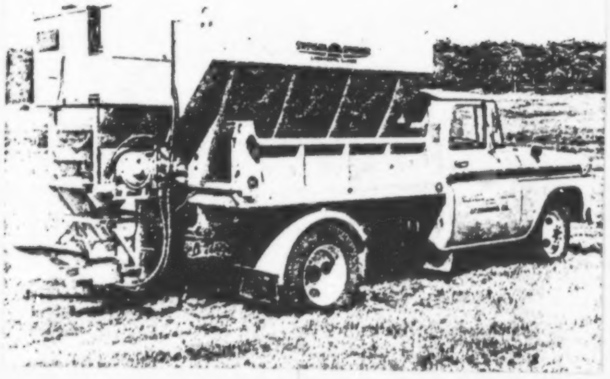

Figure 19. Standard highway centrifugal sander.
(Source: Advertisement)

Standard Hydro-Seeder*

A standard Hydro-Seeder could be used to deliver a slurry to a spill. The Hydro-Seeder is a device that is used to deliver seeds to freshly prepared highway road banks. Essentially, a centrifugal pump forces a mixture of seeds and water through a hose nozzle aimed at the desired location for the seeds. Solid particles up to 3/4-in. diameter can be sprayed with the system. The mixture can be sprayed up to 200 ft from the nozzle. The larger Hydro-Seeders can spray 3000 gal of mixtures in about 20 minutes (Figure 20).

A 3000-gal-capacity Hydro-Seeder, ready for mounting on a truck, costs about $12,000.

The Use of "Slippery Water"

Slippery water is water in which shear-reducing additive has been mixed. These additives have been used by fire departments in order to increase the range of fire hoses. The range of a hose can be nearly doubled, since the pressure drop arising from shear loss is markedly decreased.

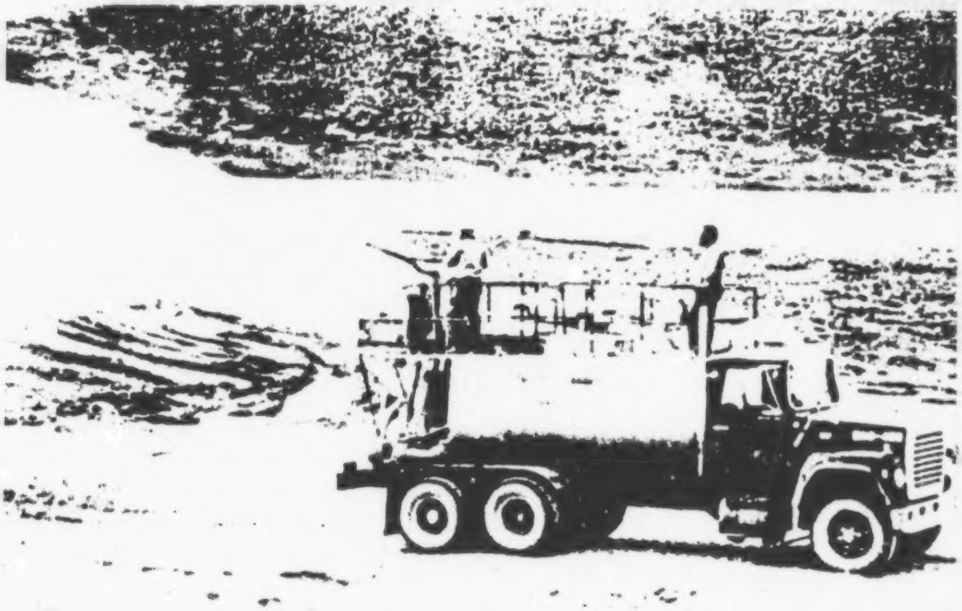

Figure 20. Commercial hydro-seeder.
(Source: Advertisement)

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* Trade name, Bowie Industries, Inc.

The use of slippery water requires the installation of a metering system to accurately mix the shear-reducing additive with the water. Such systems are typically installed directly onto fire trucks.

The cost of installing a typical wet water system on a vehicle such as a fire truck is approximately $6000.

Slurry Pumping With Existing Fire Truck Pumps and Hoses

Chemical slurries could be delivered to spills by using existing fire truck pumps, hoses, and nozzles. Fire truck pumps are usually of the centrifugal type and are intended to pump water. Pumps can usually handle liquids of viscosities up to 5000 SSV (SAE 40 motor oil at room temperature). Liquids much thicker than this usually degrade the performance of any type of pump when compared to the performance of the pump moving water. The presence of intake screens on fire truck pumps should be taken into account in considering this system. Another consideration is the possibility of fouling or corroding the fire truck pumps during or after pumping slurries.

Since this concept uses existing equipment, the only major cost would be any extra maintenance cost incurred by using this concept on the equipment.

Long Boom Deployment of Slurry Transfer Hoses

A boom arrangement could be used to deliver foam over a spill some distance from an operator. A typical truck-mounted crane equipped with a telescoping hydraulic boom could be used to position a slurry transfer hose over a spill. The slurry would be forced through the hose by a slurry pump positioned near a reservoir of slurry (Figure 21).

A telescoping truck crane with a 150-ft horizontal reach costs approximately $170,000. A suitable slurry pumping system capable of pumping up to 600 gal/min would cost approximately $35,000.

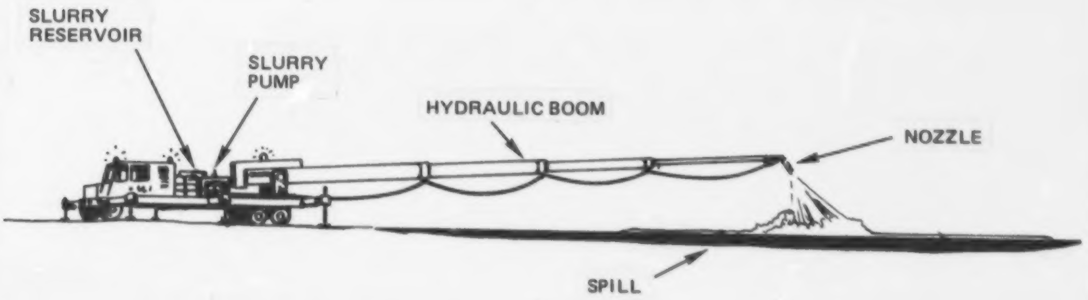

Figure 21. Slurry delivery concept by means of a truck-mounted boom.

LIQUID TRANSFER CONCEPTS

Concepts involving liquid transfer processes include water flooding and the addition of chemical neutralizers to the spill. Delivery of liquid nitrogen is a possibility for some approaches.

Pumps and Liquids From Available Fire Trucks

An obvious solution to the problem of liquid delivery to spills is the use of existing fire trucks and their liquids to cover the spill. Additives might be mixed with the liquid to enhance its "pumpability" or improve its effectiveness after it is delivered to the spill, but the main concept is to use as much standard equipment as possible.

Since existing equipment would be used, the only extra cost would be for special liquids and additives (if required) and any extra maintenance costs their use would incur.

Slippery Water Usage

The range of fire hoses can be increased by the use of shear-reducing additives. Fire departments have made use of these additives. This involves fitting a fire hose system with an additive injection/mixing device which combines the desired amount of shear-reducing additives with ordinary water.

The cost of such a system installed on a typical fire truck is $6000.

Balloon Deployment of a Liquid-Dispensing Hose Vehicle

A hose could be supported over a spill by a small balloon and the nozzle directed at the spill. Balloons have been used as support platforms in many situations. They are occasionally used to transport large objects over terrain where conventional ground-type equipment is forbidden or is not practical. Examples of this are logging operations or off-loading bulky containers from ships near shore. However, balloons have several disadvantages. They may be difficult to move from place to place. They are vulnerable in strong winds, especially the hot-air variety, and they may require several hours to set up. Reaction forces from the nozzle could be severe.

A typical helium balloon at 1000 lb lifting capacity is 33 ft in diameter and is 84 ft long when inflated. The balloon and ground support equipment cost approximately $90,000 (Figure 22).

Deployment of Hoses and Nozzles With Supporting Booms

A boom arrangement could be used to deliver liquid over a spill some distance from an operator. A truck-mounted crane equipped with a telescoping hydraulic boom could be used to position a liquid transfer hose and nozzle over a spill. The pump and hose would be furnished by fire trucks at the scene.

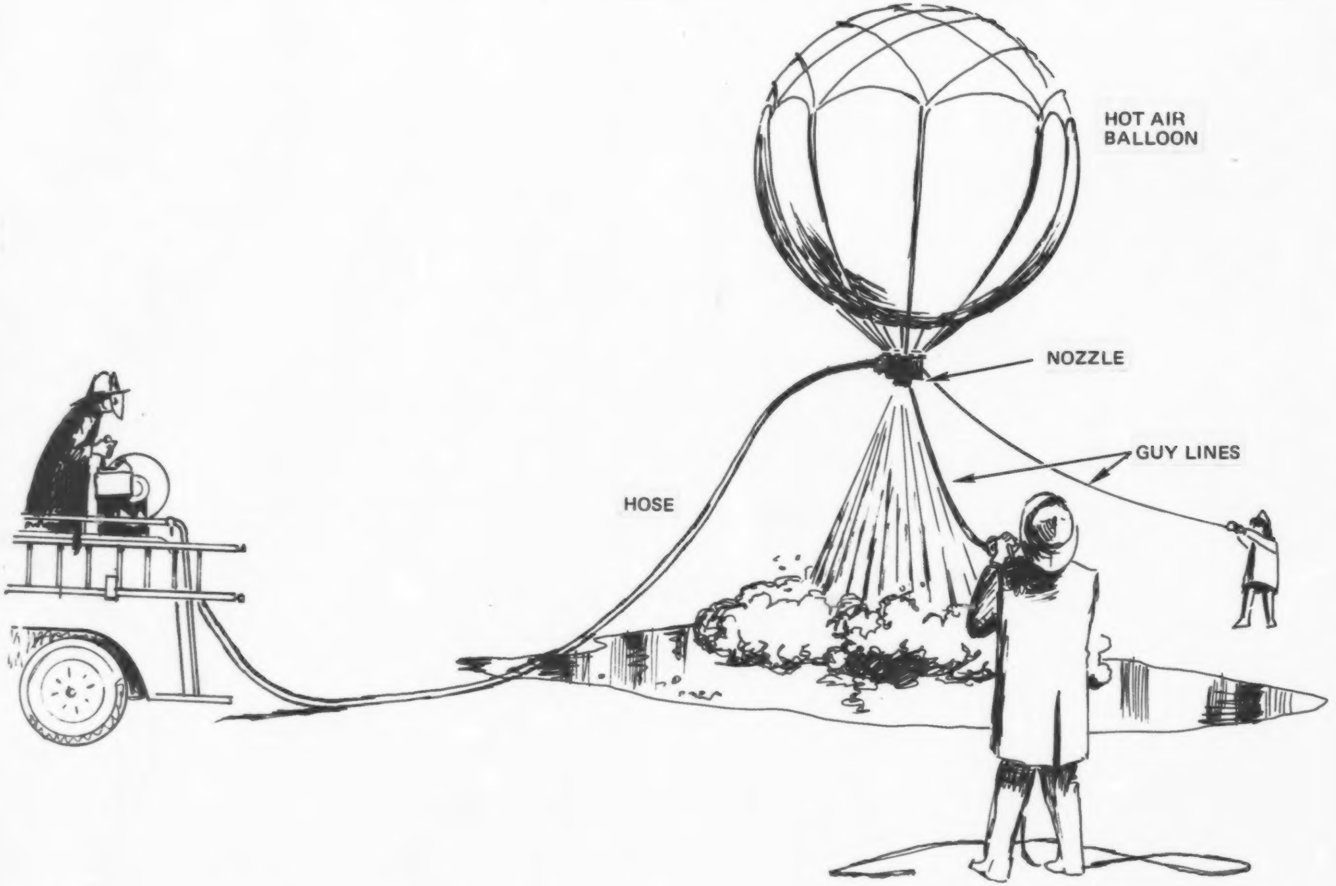

Figure 22. Hot-air balloon delivery concept.

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A typical telescoping truck crane with a 150-ft horizontal reach costs approximately $170,000.

ENERGY TRANSFER CONCEPTS

The ideas grouped under this heading explore the use of energy transfer to accelerate evaporation from spills, to ignite spills, to extinguish spill fires, and to oxidize the volatiles of spills. The purpose of increasing the spill evaporation rate is to remove any residual hazardous material, under controlled conditions, after the pool of liquid has been removed.

Flame-Throwers for Heating or Ignition of Spills

A flame-thrower might be used to heat or ignite a spill. The U.S. Army has portable flame-throwers in its inventory. The units are carried by an individual and contain 4½ gal of fuel. They weigh about 50 lb when loaded and 22 lb when empty. The maximum effective range of such devices is about 150 ft with a flame duration of 5 to 8 sec (Figure 23). Civilian flame-throwers having half the capacity and one-sixth the range of the U.S. Army units cost about $260.

Spill Heating With Infrared Radiation

Infrared lights, focused with a parabolic reflector, could be used to heat a spill site and increase the rate of evaporation. Both gas and electrically powered portable infrared heaters are available commercially. A gas-powered 32,000-BTU-per-hour gas heater costs approximately $80. A 21,000-BTU-per hour electrical heater costs approximately $160. A suitable reflector could be fabricated. Developmental costs for a prototype system have been estimated at approximately $28,000 over a period of 4 months (Figure 24).

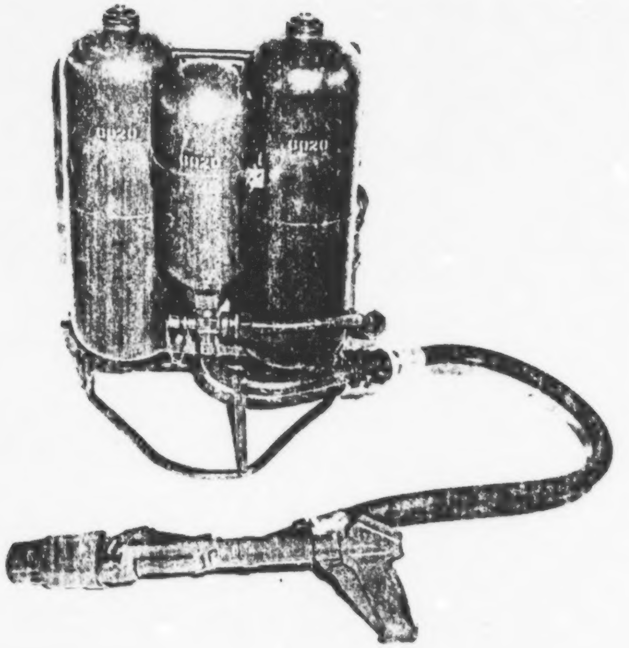
Solar Energy Lenses

Large concentrating lenses could be used to heat the chemical spill with solar energy, and thus increase the rate of evaporation. A typical scheme might involve several concentrating lenses which would only be able to focus the sun's rays upon a few small local areas at any particular time. The temperature at these points might be raised several hundred degrees, depending upon the heat transfer characteristics of the surroundings and the boiling point of the chemical spilled. The lenses could be panned about the spill so that the entire surface of the spill would have been heated, although it would not be uniform. Once the concentrated rays were removed from a particular area, however, that area could be expected to cool rapidly.

A standard type of concentrating lens that might be used in this type of situation is a Fresnel lens. They are manufactured in sizes up to about 3 ft x 15 ft. The cost of the lenses would be about $3.50/ft^2.

Sonic Disturbance or Blast

In about 10 percent of the spills, fire is involved. While the fire consumes much of the released vapor, it also causes damage to nearby cargos



UNLOADED WEIGHT AS PICTURED: 42 lb

LOADED WEIGHT (DEPENDING ON TYPE OF FUEL USED): 60-70 lb

TYPE OF FEED: FUEL PROPELLED BY GAS UNDER PRESSURE.

METHOD OF OPERATION: MANUAL.

DURATION OF FIRE: CONTINUOUS DISCHARGE 8-9 seconds.

MAXIMUM EFFECTIVE RANGE: 20-25 meters UNTHICKENED FUEL.
40-50 meters THICKENED FUEL.

REMARKS: OPERATING CAPACITY 4-1/2 - 4-3/4 gallons OF FUEL WEIGHING 25 TO lb. THIS FLAME THROWER IS STANDARD B. MAY BE FIRED EFFECTIVELY AT TEMPERATURES AS LOW AS -26°F.

AN ALTERNATIVE TO THIS IS THE M202/M74 FLAME SYSTEM WITH A RANGE OF 200 yards.

Figure 23. Commercial flame-thrower.

(Source: Dept. Army Manual)

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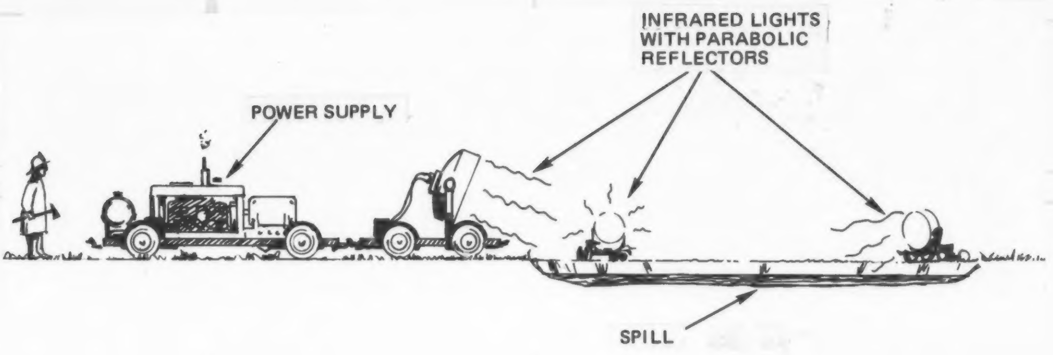
INFRARED LIGHTS WITH PARABOLIC REFLECTORS
POWER SUPPLY
SPILL

Figure 24. Infrared heating concept.

and may cause the release of more chemicals. Thus, under many spill situations, it is desirable to extinguish the fire.

The effect of an explosion or the sonic boom of a jet might be utilized to blow out a burning spill. An explosive charge could be deployed directly above the chemical spill by lowering it with a crane. The charge could then be detonated to either jar the spill or, in cases of burning spills, to put out the flame. This procedure would be similar to one used in putting out fires in oil fields.

Material and equipment costs for putting out a fire in this manner should be negligible compared to labor costs.

Standard Heat Exchanger System

A standard heat exchanger system could be developed for increasing the temperature of a spill, thus increasing the evaporation rate. A typical system might consist of a pump, a boiler, a heat exchanger, and some tubing. The spilled liquid would be heated up in the heat exchanger and then recirculated into the spill to raise the overall temperature of the fluid. This type of system has been studied for possible use in the off-loading of oil tankers. The materials for the pump, the heat exchanger, and the tubing must be selected to withstand the corrosive nature of some of the chemicals.

Costs for this type of a system have been estimated at approximately \$10-\$12 per 1000 BTU/hour. These estimated rates are based on standard systems with capacities in the range of 100,000 to 1,000,000 BTU/hour. Fuel costs should be relatively insignificant (Figure 25).

Microwave Transmitters

Microwave energy could be used to heat and evaporate the spill. Microwave energy is quickly dissipated unless it is projected into an area with a high degree of reflection. For this reason, infrared projectors would appear

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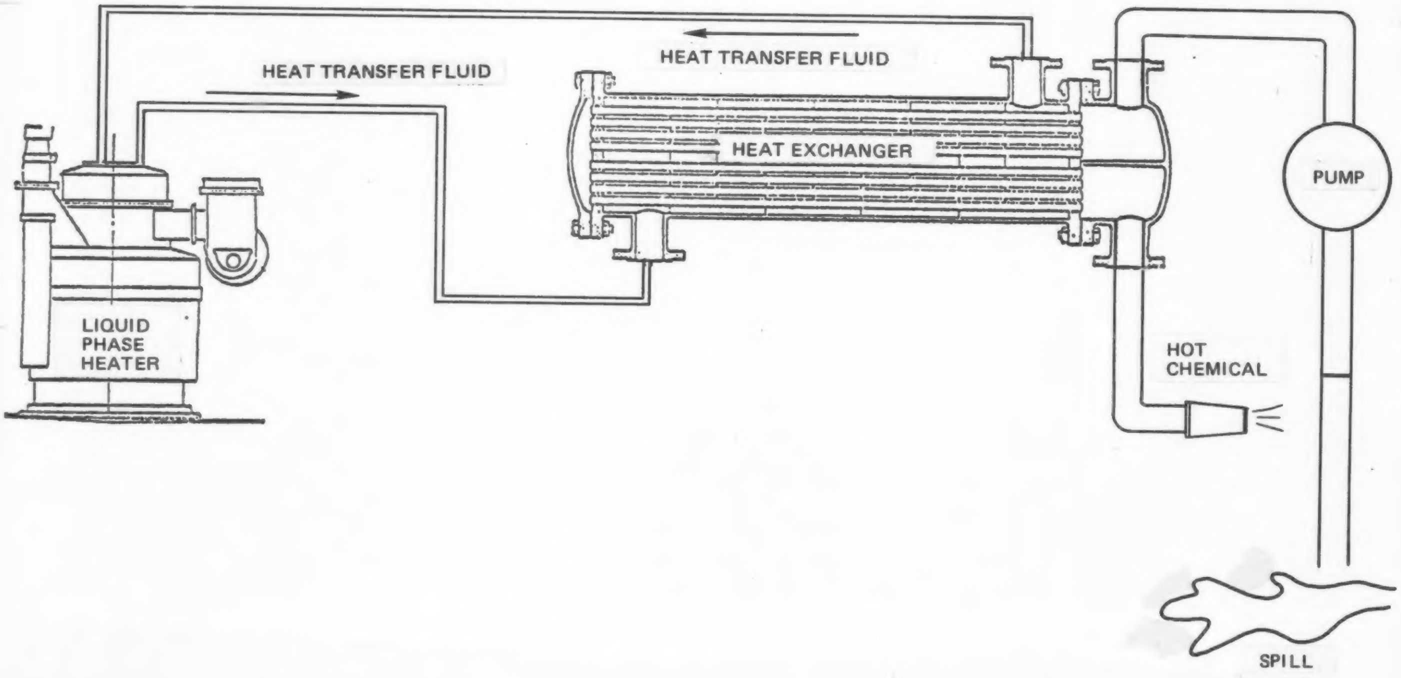

Figure 25. Heat exchanger concept.

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to be much superior to microwaves. (Use of infrared lights was the second concept listed under energy transfer.)

Incendiary Bombs

A standard, commercially-available incendiary mixture, such as thermite, could be spread over the spill and ignited. The combustion of the thermite would achieve temperatures of approximately 3300°F for a short period of time. About half of the incendiary metal (by weight) would be left after ignition.

A typical thermite reaction has an approximate specific energy ratio of 50 BTU/pound. The cost of thermite is about 55¢/lb, resulting in an approximate cost of 1¢/BTU.

Standard Cooling Equipment

A standard heat exchanger system could be adapted for use in decreasing the temperature of a chemical spill. Such a system might involve a pump, a refrigeration unit, a heat exchanger, and some tubing. The liquid chemical would be pumped through the heat exchanger, where it would be cooled, and then sprayed back into the pool to lower the overall temperature of the spill. This scheme is similar to the one discussed for raising the temperature of the spills. The materials for the pump, the heat exchanger, and the tubing would have to withstand the corrosive nature of some of the chemicals.

Costs for this type of system have been estimated at approximately $50 per 1000 BTU/hr.

Air Curtain Destructor Devices

The hazardous chemical spill could be drawn off into trenches at a controlled rate. Air curtain destructor devices could then be emplaced over the trenches to ignite the chemical vapors. A super-charging air curtain causes the vapors to burn rapidly with little or no smoke emission.

Portable air curtain destructors are commercially available in 21- or 42-ft lengths. The cost of a 21-ft unit with a diesel engine drive would be $13,600 (Figure 26).

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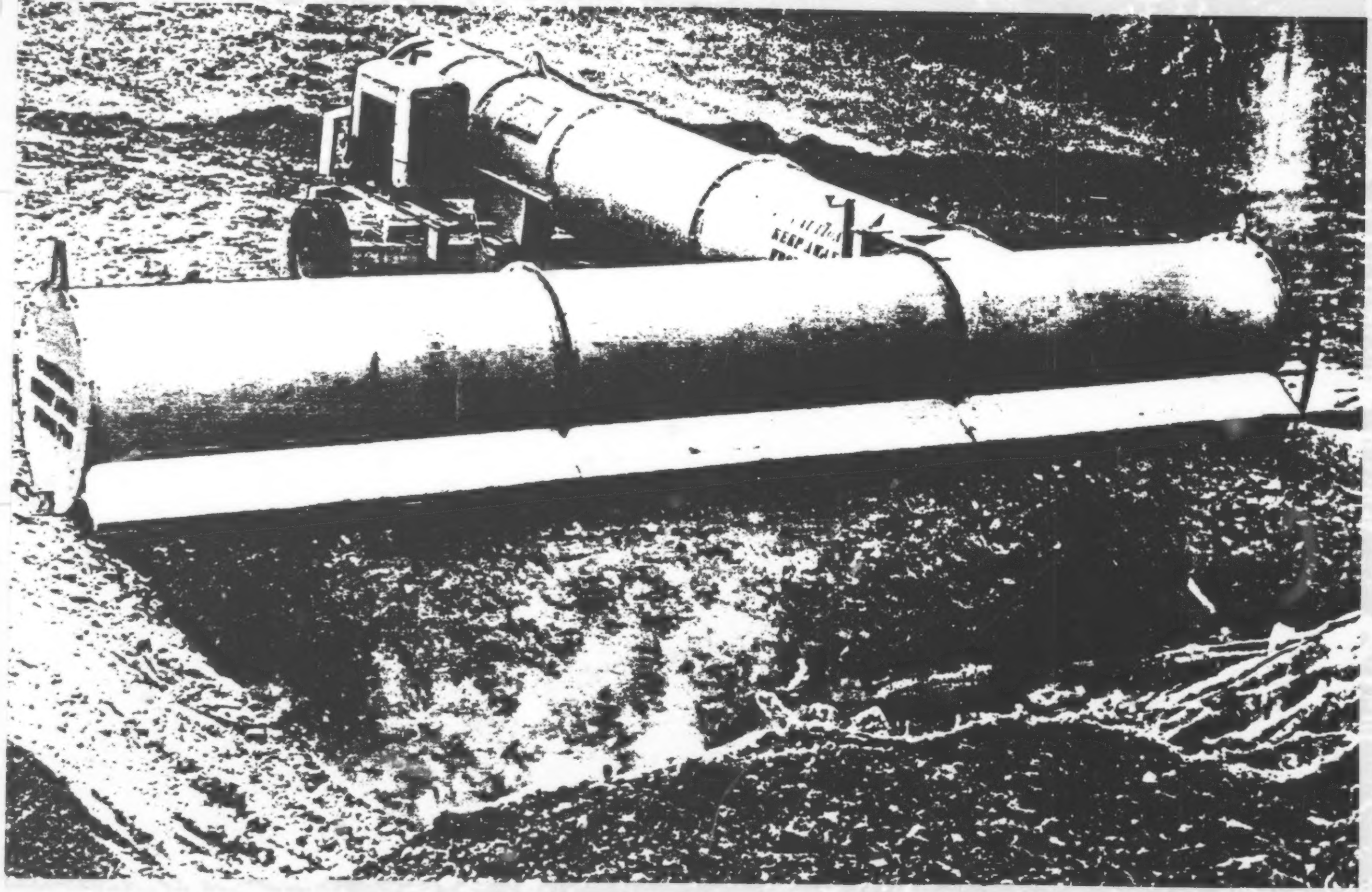

Figure 26. Air curtain destructor.

(Source: Advertisement)

SECTION 7

SCENARIOS UTILIZING NEW CONCEPTS

The situations described in this section were compiled from actual field experiences of the Battelle-Columbus staff. The intention here is to assemble and compare the currently employed procedures for combatting volatile hazardous spills on land with potential control concepts that could be "the better way" if further developed.

The spill scenarios that are included in this section occur frequently in the heavily industrialized states and their occurrence in the future is highly probable. The scenarios are exemplary and should not be construed as presenting the _only_ spill control techniques that were actually attempted and/or were successful.

It has been found that in practice, response teams have utilized combinations of vapor suppression techniques to fit the variations of the physical field setting. In all scenarios selected, the safety of the cleanup crews was of paramount concern.

LPG*-DIFFUSION FROM UNDERGROUND PIPE

Situation

A report has been received from a volunteer fire department that they are obtaining explosive values on their monitoring equipment in basements of homes in a semi-rural area. It was rapidly determined that the gas was diffusing to the surface along a ditch in front of the homes. An LPG pipeline marker is nearby. A call to the company operating the pipeline reveals that they had an automatic shutdown during the night before and they are walking the line to find the break. Fumes are flowing heavily from the ditch.

Ambient Conditions

The surface air is calm and a conduction fog is blanketing the area. The terrain is flat, with repeating surfaces of sand, gravel, and alluvium making up the site soils. The wells in the area are venting gas.

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* Liquefied Petroleum Gases

Problem

The highway has been closed and the neighborhood evacuated for an unknown period of time. Explosions have occurred in some basements.

Current Response

Using explosion-proof core drilling rigs, numerous shallow shafts have been drilled and fitted with flaring ignition systems to burn off, at height, the permeating gas with the logic of "WICKING" the gas to the flames.

Proposed New Technology

Option I--

After the gas main has been shut down, upstream trenches should be dug into the lens where the sand and gravel surface. A slightly modified sandblasting pump is utilized to blanket the bottom of the trench with 1/8-in.-diameter dry ice pellets. The flashpoint should drop considerably. The CO_2 sublimes and fills the trench bottom. Since the CO_2 is a gaseous blanket, the natural gas can vent slowly but under greatly reduced ambient air release rates.

Option II--

After determining the subsurface piezometric gradient, several shallow injection wells are drilled up the geologic gradient and away from the permeating natural gas. Fresh water is metered into the receiving formation. The advancing permeation of the water will increase the rate of methane gas migration into the wicking flare stacks as described in the Current Response description.

Option III--

Increase the rate of gas emission from the deep trenches by utilizing infrared lights (explosion-proof) with parabolic reflectors to heat the trench walls to further increase the volatility. Above these trenches, large fans (commonly used to abate smoke damage in buildings that have had a fire) are directed to provide dilution and direction to the plume. Convection currents are established in the trench to create a "chimney" draft effect.

STREAMING-VOLATILIZING ACRYLONITRILE TANK CAR (RAILROAD)

Situation

Because of a humping yard accident, the dome cover and valves of a 5000-gal tank car have been sheared and acrylonitrile is streaming into the railroad bed ballast and drainage channels adjacent to the facility.

Ambient Conditions

It is an extremely hot day and the humping yard temperature is about 110°F. The fumes are being blown at a velocity of 1.5 to 5 m/s (3 to 10 knots) directly toward a grain-processing warehouse facility. The spill is dammed in a concrete-lined ditch.

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Current Response

Even though ignition has not occurred, the local fire brigade of the railroad is directing 2 deluge (6-inch) hoses at the emitting opening of the tank car, which is nearly upside down. Another fire-fighting unit is covering the pools of acrylonitrile with sand. The earthmoving equipment operators are being subjected to extreme danger.

Proposed New Technology

A large helicopter drops a large parachute of Hypalon* material to cover the tank car. The bottom of the parachute is equipped with 6-in.-diameter light canvas hose. Through this hose system liquid nitrogen is pumped into the chute and inundates the plumbing system of the tank car. Eventually, with the added insulation of the chute, the tank car plumbing will be frozen and the acrylonitrile will be frozen in place. Volatilization is greatly reduced. The response time for helicopter-aided deployment of the covers in spill response circumstances has been less than 2 hours.

MASSIVE GASOLINE SPILL - BULK FARM

Situation

Due to a "computer" error, an additional 80,000 gal of gasoline were piped into a full tank. The subsequent overfill, which occurred during the night, nearly filled the dikes surrounding the tank and volatilized rapidly.

Ambient Conditions

An air stagnation condition covers the local area. Explosive mixtures of gasoline-air are gathering in many pockets and buildings. Sunlight is intense and the volatilization is rapid. Several trenches and sumps are gathering previous gasoline runoff that created the dikes.

Current Response

A concerted effort is being made to re-load the spilled gasoline into waste-oil tanks. The local fire department is applying various depths of protein-based foams to the surface of the pool of gasoline. The perimeter of the spill zone is being flushed with open hydrants and a sheen of gasoline can be seen flowing into a storm drain and into a creek.

Proposed New Technology

Option I--

Several vacuum-siphon lines are placed in the gasoline by using booms of aerial fire ladders. The dike zone is treated with large blocks of dry ice delivered by a four-bar linkage device. The gasoline spill is then blanketed

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* DuPont trade name.

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with dry ice pellets delivered by a continuous air cannon device. Tarpaulins are deployed over the dike zone utilizing remotely operated aerial ladder equipment. Once a vapor shield of CO_2 has formed under the tarpaulin, the air vacuum pumps can begin operation to remove the cold gasoline. The time necessary to complete the above option is estimated at less than one hour.

Option II--

Utilizing two or more Silage blowers with a mulching machine, layers of pulverized straw or peat could blanket the spill and insulate as well as absorb a significant percentage of the spilled gasoline. Rates of application could approximate 5000 lb/min.

Option III--

To limit the surface area of the gasoline spilled, the gasoline could be encircled by quick-setting semi-solid foams. Such efforts could be accomplished in less than 20 minutes if the equipment were readily available to the spill contractor or fire departments.

VENTING INDUSTRIAL SUMP - HYDROGEN SULFIDE

Situation

At a local rendering plant located in a congested industrial park, a large outdoor sump is generating repeating pulses of hydrogen sulfide gas (H_2S). Anaerobic decomposition is evident in the mechanically-mixed sump tank. Several firemen have been injured.

Ambient Conditions

The sump is partially enclosed by the roof of an open-air receiving dock. However, a gentle breeze of 3 to 5 knots is blowing the H_2S toward several nearby industries. The sump has concrete walls.

Current Response

The remaining firemen evacuate the premises and direct several forced-air-blowing and exhausting fans over the sump. Water was initially added to the bubbling fluid in the pit, but soon afterward it seemed to increase the rate of H_2S emission.

Proposed New Technology

The fluid in the sump has been depleted of oxygen and the system has gone anaerobic. Large quantities of air or oxygen should be bubbled through the sump in an attempt to re-establish an aerobic process.

BURNING PESTICIDE WAREHOUSE, HCN, PHOSGENE, ETC.

Situation

After a fire fed by tanks of xylene and toluene, a warehouse containing 340 tons of mixed pesticides has been reduced to a smoldering ruin. Fumes from the destroyed warehouse are being blown across the street into a residential neighborhood and are also enveloping a small hospital. The winds are variable and the plume trails and loops along the surface. Approximately 140 people have been treated at surrounding hospitals for the toxic fume inhalation. Runoff has contaminated a water supply reservoir. Massive fishkills are in progress. The city's water intake has been shut off. The walls and roof of the warehouse have totally collapsed.

Ambient Condition

It is a cool summer night and the smoldering debris has been determined to lie upon an intact concrete floor area. Runoff waters have flooded the streets and curbs of the formulating and packaging plant. The terrain is generally flat.

Current Response

The several fire departments have been spraying the debris with even more water and are maintaining the evacuation status.

Proposed New Technology

Option I--

Utilizing large helicopters, several fireproof tarpaulins are deployed over the debris pile in an upside-down parachute attitude. The chutes are lined radially with canvas hose lines with gas defuser webbing near the center of the circular tarpaulins. High-pressure induction fans blow liquid nitrogen through the tarpaulins. The cryogen filters through and chills the once-smoldering pesticide-laden ashes. The toxic fumes are no longer generated and the liquid pesticide-laden runoff is frozen. After several hours of treatment, the solid frozen mass could be loaded into covered waste disposal trucks for additional treatment, encapsulation, etc.

Option II--

Several large industrial sandblaster units can be loaded with dry ice pellets crushed to about 1/8-in. diameter and used to blanket the smoldering pesticide-laden debris with several inches of dry ice pellets. Fireproof tarpaulins are then pulled over the rubble to provide insulation. A marked reduction in fume generation should result.

Option III--

The pesticide-laden rubble could be smothered with earth carried in by large payloaders. Soil from nearby sites could be used to bury the piles of smoldering chemicals. It is estimated that approximately 20 tons of soil could be moved and dumped on the rubble in less than 2 hours.

NATURAL GAS - PIPELINE RUPTURE — ABOVE GROUND

Situation

Because of a hillside slump, a 6-in.-diameter natural gas pipeline has ruptured and is exposed on a slope above a secondary road in the small valley below. The road is closed to traffic. Some birds and other small wildlife have died in the plume.

Ambient Conditions

There is a downhill convection of the methane and the gas is flowing under a canopy of trees.

Current Response

Attempts are made to find the upstream shutoff valves while the fire department plays a remote deluge hose upon the leak.

Proposed New Technology

A cyano-acrylate film is applied over the spill with a 3-in.-diameter pressure hose fitted with a small acid atomizer providing a slight acid medium for the film to form upon. The ruptured pipe end is simply covered by a mound of film that sets up in less than 45 seconds. The methane is held in place by the pipe until back pressure can be applied to vacuum the methane out of the line. The material is applied with a piece of equipment similar to Figure 11.

PHOSGENE GAS EMISSION - INDUSTRIAL SOURCE

Situation

In a basement storage room a 1-ton cylinder of phosgene gas is venting phosgene from a defective seal. The chamber's ventilating system is pumping phosgene gas out of several ports. The light yellow gas is rolling down a streetside curb and into storm sewer drains.

Ambient Conditions

The humidity is high and the emission has occurred during a light rain.

Current Response

A mist nozzle is used to spray water on the cylinder dome cap but the phosgene is still moving out of the room.

Proposed New Technology

Option I--

The phosgene cylinder is packed in dry ice to lower the temperature and pressure of the phosgene. A large spray aerosol can of cyano-acrylate is sprayed on the leaking seals to form a solid film cover to retard the leakage of phosgene gas.

Option II--

A high-pressure slurry of 30 percent lime is directed on the leaking cylinder to adsorb and react with the phosgene. The phosgene is in effect scrubbed from the air and partially neutralized (Figure 22).

Option III--
To reduce the leak rate and the concentration of phosgene, the cylinder could be placed on its side and the room flooded with a water slurry of activated carbon. With hose attachments the water-carbon slurry could be pumped by a modification of the design of a commercial hydro-seeder. (Figure 21)

SILICON TETRACHLORIDE BULK TANK LEAK

Situation

In a heavy industrial area an 800,000-gal bulk tank of silicon tetrachloride ($SiCl_4$) began venting deadly clouds of HCl vapors.

Ambient Conditions

The meteorological conditions were stagnant with 2- to 4-mph winds. A large pool of hydrochloric acid accumulated in diked areas around the tank's offloading zone.

Current Response

The diked area was blanketed with sand, then with lime, and then with #6 heating oil. As a last resort, a quick-setting concrete was dumped on the plumbing system in an attempt to seal the pipe leak.

Proposed New Technology

Option I--
Trenches can be dug inside the diked area to gather the $SiCl_4$ in sumps. This will greatly reduce the area of volatilization. With a modified snow blower, several inches of pelletized dry ice are spread on the chemical. At the source of the spill, the pipe gallery, a hood or tent is lowered over the spill by the boom of an aerial fire truck. Styrofoam blocks are added to the bottom of this makeshift tent or hood. Liquid nitrogen is then fed over the aerial ladder and into the hood area over the leaking pipe. The $SiCl_4$ will rapidly freeze solid and plug any further emission. The remaining volumes could be offloaded into appropriate tank trucks, railroad cars, etc. It will be necessary to bleed the refrigerant liquid nitrogen over the frozen pipe gallery to maintain its cryogenic property. The rate of emission over the ponded chemical will greatly reduce the escape of the hazardous gas.

Option II--
High-speed conveyor belts can be utilized to load dry ice into the tank through the roof vents of the tank to reduce the temperature of the $SiCl_4$. This will lower the rate of vaporization of the $SiCl_4$.

Option III--
Construct a prefabricated acid-resistant dome. This acid-resistant material could be very plastic and flexible in nature. Erection of the dome could

be assisted by forced-air pumps and fans. Once this dome or tunnel configuration is placed over and against the pipe gallery, this structure would insulate and provide a limited exposure area for both the $SiCl_4$ and the coolant (LN_2, dry ice, etc.).

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